



TRI-STATE GENERATION AND TRANSMISSION ASSOCIATION, INC.

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January 13, 2000

Mr. William Grimley
Attn: Electric Utility Steam Generating Unit
Mercury Test Program
Emissions Measurement Center
Interstate 40 and Page Road
4930 Old Page Road
Room Number E-108
Durham, North Carolina 27709

RE: Craig Unit 1 and Craig Unit 3 Mercury Speciation
Stack Sampling Test Reports

Dear Mr. Grimley:

Enclosed for your approval are three (3) copies each (one (1) each unbound) of the referenced reports. Please call me at 303-452-6111 if you have any questions.

Sincerely,

Ed Lasnik
Senior Engineer
Environmental Services

EL:r

Enclosures



MERCURY SPECIATION STACK SAMPLING TEST REPORT: CRAIG STATION UNIT 1

January 2000

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INTRODUCTION

1.1 Summary of Test Program

Purpose of Test

The United States Environmental Protection Agency (EPA) has implemented an Information Collection Request (ICR) aimed at characterizing mercury emissions from coal-fired power plants in the United States. As part of this ICR, the operators of selected coal-fired boilers were required to collect and analyze flue gas samples for particulate, elemental, and oxidized mercury.

Tri-State Generation and Transmission's (Tri-State's) Craig Unit 1 was selected at random by the EPA to provide speciated mercury emissions data, which will then be used to develop emission factors for boilers in its class.

Measurements collected were speciated mercury emissions at the stack, speciated mercury concentrations at the inlet of the boiler's last air pollution control device (a wet limestone scrubber), and fuel mercury, chlorine, moisture, sulfur, ash, and heating value.

Test Unit

The test unit is Craig 1. This unit is operated by Tri-State Generation and Transmission Association (Tri-State), and is located in Craig, Colorado. The unit was selected by the EPA as part of the following category:

- Fuel type: subbituminous
- SO₂ control type: wet scrubber
- Particulate control type: hot side electrostatic precipitator (ESP)

The unit is rated at 456 MW gross. Craig 1 is a Babcock & Wilcox opposed-fired boiler, with original equipment low-NO_x burners for NO_x control. It fires a blend of local low sulfur subbituminous coals from the Trapper and Colowyo mines. SO₂ emissions are controlled by limestone wet scrubbers.

Test Measurements

The program included the following tests, with triplicate sets of measurements performed simultaneously at each test location:

- Particulate, oxidized, and elemental mercury emissions at the stack per the Ontario Hydro mercury speciation method.
- Particulate, oxidized, and elemental mercury concentrations at one of two air preheater exit ducts. This location, referred to as the “inlet”, is downstream of the hot side electrostatic precipitators and upstream of the wet scrubbers.
- Mercury and chlorine content of representative coal samples collected from the coal feeders.
- Coal moisture, sulfur, ash, and heating content.

Responsible Organizations

Responsible organizations for this project are:

- Test site operator: Tri-State
- Program sponsor: Electric Power Research Institute (EPRI)
- Sampling team: Fossil Energy Research Corp. under contract to EPRI, with Delta Air Quality Services as a major subcontractor
- Sample analysis: Philip Analytical Services (flue gas mercury, coal chlorine), Commercial Testing and Engineering (coal HHV, S, ash, moisture), Frontier Geosciences (coal mercury)

Dates of Test

The test program was conducted on September 27-29, 1999. Daily activities included:

- September 27: set up and conducted field blanks.
- September 28: conducted Runs 1 and 2.
- September 29: conducted Run 3.

Document Description

This document is the test report for the Craig Unit 1 mercury ICR testing. It has been prepared in accordance with Emission Measurement Center Guideline Document GD-043, as required in the ICR.

The work described here is based on the Craig Unit 1 Test Plan (Report No. FERCo R674), the Craig Unit 1 Quality Assurance Plan (Report No. FERCo R697), and the Craig Unit 1 Test Plan Addendum (Report No. FERCo R721). These reports are available from Tri-State, the EPA or FERCo.

The Test Plan Addendum was prepared in response to initial EPA review of the Test Plan. The Test Plan Addendum was approved by Mr. William Grimley of the EPA. The QA Plan was approved by Ms. Lara Autry of the EPA prior to testing. EPA comments on the draft QA Plan were incorporated into the final version of the QA Plan.

1.2 Key Personnel

Table 1-1 lists the test program organization and key individuals with responsibilities, phone numbers, and e-mail addresses. A program organizational chart is shown in Figure 1-1.

The program was jointly funded by Tri-State and EPRI. FERCo was under contract to EPRI. The Project Quality Assurance Officer was Greg Quartucy of FERCo, who reported directly to Larry Muzio, FERCo's Vice President. External QA activities were performed by Dennis Laudal of UNDEERC. Mr. Laudal reported directly to Paul Chu of EPRI. Both UNDEERC and FERCo are contractors to EPRI. The reporting function from Mr. Laudal to Mr. Chu is considered to be external to FERCo's project.

Mr. Lasnik, Mr. McDannel, and Ms. Bell were all on-site for the testing. There were no observers from regulatory agencies.

Table 1-1. Test Program Organization and Responsibilities

Organization	Individual	Responsibility	Reports To	Phone Number	Fax Number	E-mail Address
Project Management and Oversight						
EPRI	Paul Chu	EPRI Project Manager	N/A	(650) 855-2812	(650) 855-2619	pchu@epri.com
FERCo	Lawrence Muzio	Vice President	N/A	(949) 859-4466	(949) 859-7916	lmuzio@ferco.com
FERCo	Greg Quartucy	QA Manager	Lawrence Muzio	(949) 859-4466	(949) 859-7916	gquartucy@ferco.com
Host Utility						
Tri-States	Ed Lasnik	Program Coordinator and Site Contact	N/A	(303) 452-6111 x6173	(303) 254-6013	edlasn@tristategt.org
FERCo/Delta Sampling Team						
FERCo	Mark McDannel	Program Manager	Paul Chu	(949) 859-4466	(949) 859-7916	mmcdannel@ferco.com
Delta	Arlene Bell	Project Chemist	Mark McDannel	(714) 279-6777	(714) 279-6781	deltaaqs@aol.com
Philip Environmental	Ron McLeod	Sample Analyses	Mark McDannel	(905) 332-8788	(905) 332-9169	rmcleod@philipinc.com
External QA/QC						
UNDEERC	Dennis Laudal	External QA/QC	Paul Chu	(701) 777-5138	(701) 777-5181	dlaudal@eerc.und.nodak.edu

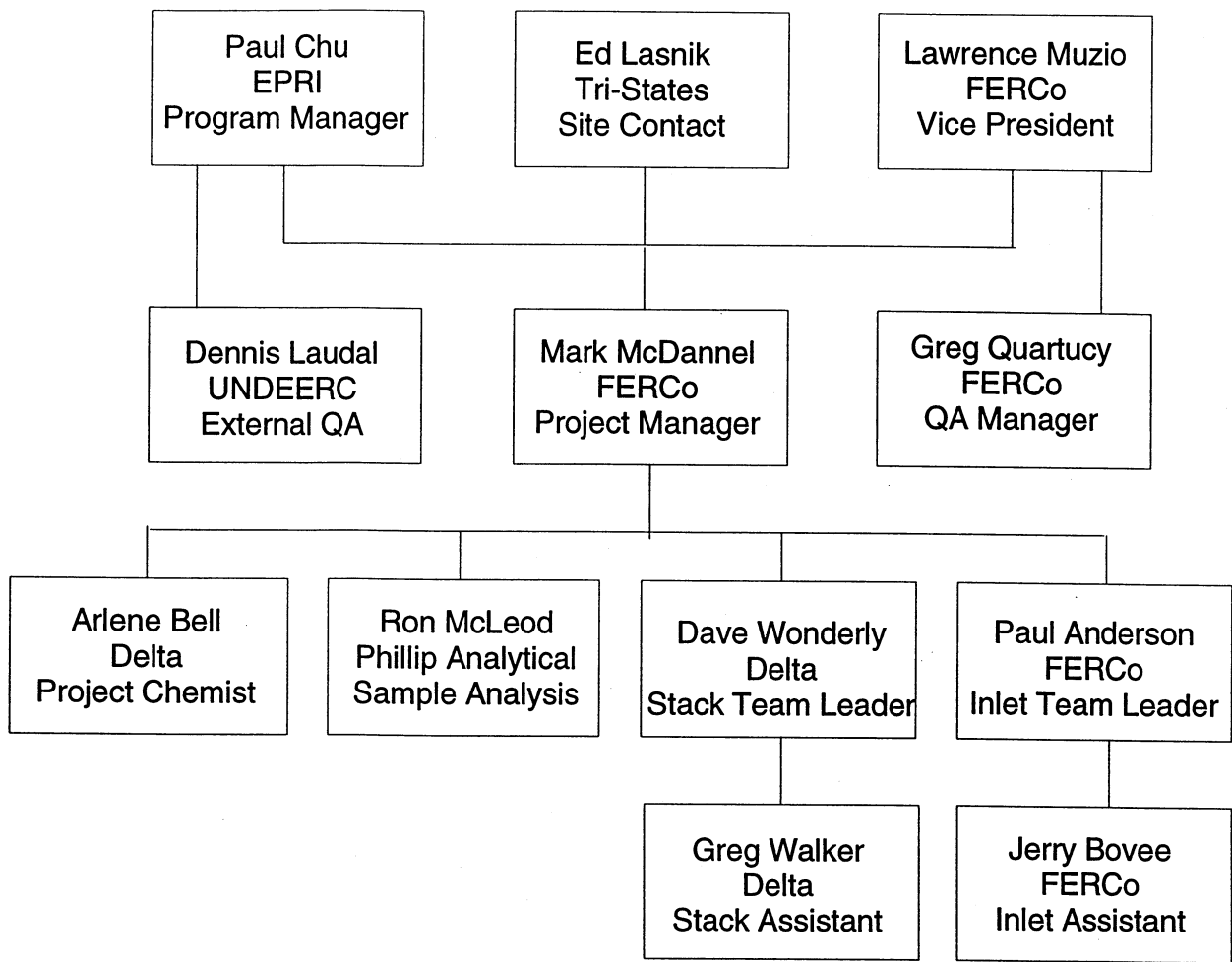


Figure 1-1. Project Organization Chart

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PLANT AND SAMPLING LOCATION DESCRIPTIONS

2.1 Process and Control Equipment Description and Operation

Craig 1 is an opposed-fired Babcock & Wilcox boiler rated at 456 MW gross. Figure 2-1 shows a schematic of the boiler and pollution control equipment, including sample points.

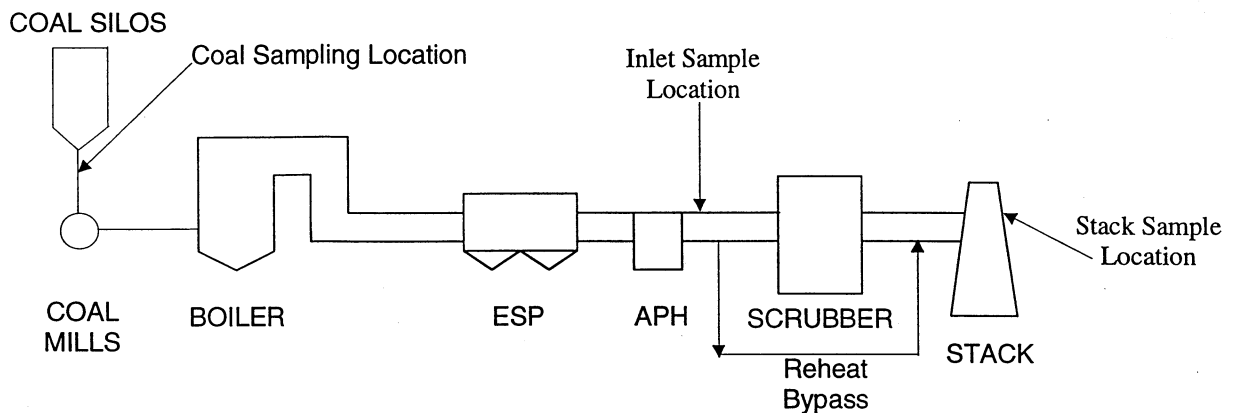


Figure 2-1. Craig Unit 1 Schematic

Key unit parameters include:

- Unit capacity: 456 MW gross
- Boiler type: Babcock & Wilcox, opposed-fired, balanced draft
- Fuel type: subbituminous, from Trapper mine (0.36% S) and Colowyo mine (0.5% S)
- SO₂ control: limestone wet scrubber. Typically, either two or three of the four scrubber modules are in service, and approximately 20% of the boiler exhaust gas is bypassed around the scrubber to provide reheat for the stack gases. The scrubber is controlled to maintain stack SO₂ levels of 0.3 lb/MMBtu or less.
- Particulate control: hot side ESP, SCA 130 ft³/kacfm, 99.9% efficiency
- NO_x control: original equipment low NO_x burners

Fuel samples were collected at the coal feeders ahead of the boiler, inlet samples were collected at the inlet to the wet scrubber, and outlet samples were collected at the stack.

The sample gas at the inlet is approximately 250°F. At the stack, the gas temperature is approximately 145°F.

Unit operation during testing was at or near nominal full load, at steady state operation. Coal type, boiler operation, and control device operation were all within normal operating ranges. Three of the four scrubber modules were in service for the tests.

Table 2-1 presents a summary of unit operation during the tests. Additional detailed unit data is included in Appendix G.

2.2 Flue Gas Sampling Locations

Table 2-2 presents a summary of key inlet and stack sample location parameters. Individual discussions of the two locations are presented below.

Inlet Locations

The inlet samples were collected at the outlet duct of one of two air preheaters on Craig 1. The original intent, as described in the Test Plan, was to sample from both air preheater outlet ducts. However, during set up it was determined that overhead obstructions on the west duct precluded sample probe access. Therefore, sampling was performed only in the east duct. Testing one of two inlet ducts is consistent with ICR procedures.

Drawings of one air preheater location are shown in Figures 2-2a and 2-2b. Flue gas from the boiler exits through two air preheaters, travels through a 25-foot long duct from each air preheater, enters a plenum, and then travels to the operating scrubber modules through inlet ducts to each module. The air preheater exit ducts were chosen over the individual scrubber module inlet ducts because access to the inlet ducts is from the side and the ducts are 33 feet wide.

Five of ten ports were used. As shown in Figure 2-2b, the 3rd port from the east was used as Port E rather than the 2nd port from the east, because the 1st and 2nd ports were not available. Because of the uniform velocity profile and the fact that no particulate mercury was detected, this change is considered to have no impact on the results.

This location does not meet the requirements of EPA Method 1, since it is less than 2 diameters downstream of the nearest flow disturbance. There were no alternate inlet locations that would have met Method 1 requirements. Cyclonic flow tests were performed in both air preheater exit ducts prior to mercury sampling. The average cyclonic flow angle was 3 degrees, with no points having a cyclonic flow angle greater than 20 degrees.

Stack Location

The stack samples were collected at the existing stack sample ports. A schematic and cross section of the stack location is shown in Figure 2-3.

Table 2-1. Summary of Craig Unit 1 Operation

	Run 1	Run 2	Run 3
Date, 1999	28-Sep	28-Sep	29-Sep
Start time	0824	1230	0820
Stop time	1148	1512	1126
Unit load, MW Net	417	417	415
Coal mills in service	All 5	All 5	All 5
Coal flow, klb/hr	408	414	418
Boiler O ₂ , %	3.3	3.2	3.3
Air preheater inlet gas temp, F	656	663	655
CEMS data			
CO ₂ , % wet	11.6	11.7	10.9
SO ₂ , lb/mmBtu	0.30	0.29	0.24
NO _x , lb/mmBtu	0.34	0.33	0.30
Opacity, %	7.8	7.4	10.8
Stack flow, kwscfh	65,500	66,300	66,700
ESP data			
Power level, kW	241	243	202
No. of sections in service	73	73	55
No. of sections out of service	7	7	25
Scrubber Data			
Scrubbers in service	A,B,C	A,B,C	A,B,C
Scrubbers out of service	D	D	D
Scrubber A			
Slurry flow, gal/min	10	12	17
Mixed gas temperature, F	140	140	140
Pressure drop, iwg	2.8	3.1	4.7
Reheat bypass damper, %	28	26	23
Scrubber B			
Slurry flow, gal/min	12	12	12
Mixed gas temperature, F	140	140	140
Pressure drop, iwg	1.3	1.3	1.4
Reheat bypass damper, %	30	28	25
Scrubber C			
Slurry flow, gal/min	13	14	12
Mixed gas temperature, F	140	140	140
Pressure drop, iwg	1.9	1.9	1.9
Reheat bypass damper, %	19	16	12

Table 2-2. Craig Unit 1 Sampling Location Descriptions

	Inlet	Stack
	East APH outlet duct	Stack platform
Elevation	Approximately 100'	300'
Physical access	Elevator, stairs	Elevator
Side or top access	Top	Side
Round or rectangular	Rectangular	Round
Port length (outside of port to inner stack wall)	18"	18"
Number/type of ports	Five 4-inch w/ flanges per duct	Four 4-inch w/ threaded plugs
Inside dimensions	8' 3" deep x 32' 10" wide	27' 11.6" ID
Nearest upstream disturbance		
Disturbance	Right angle turn	Duct entrance
Distance, ft	13'	200'
Distance, diameters	1.0	8
Nearest downstream disturbance		
Disturbance	Entrance to plenum	Stack exit
Distance, ft	12'	300'
Distance, diameters	0.9	11

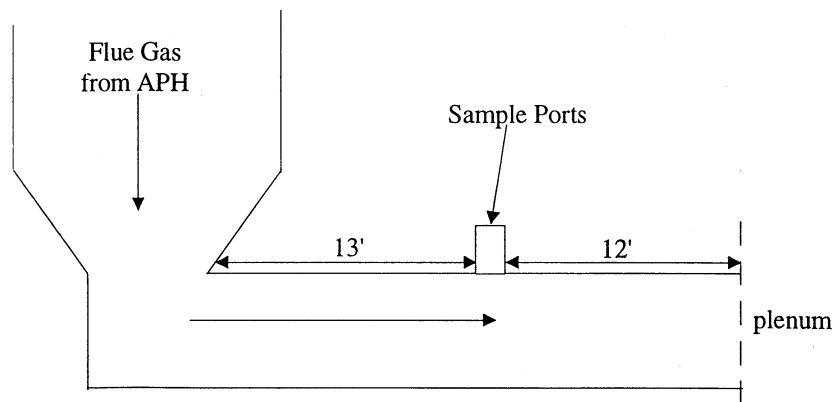


Figure 2-2a. Craig Unit 1 Inlet Sampling Location

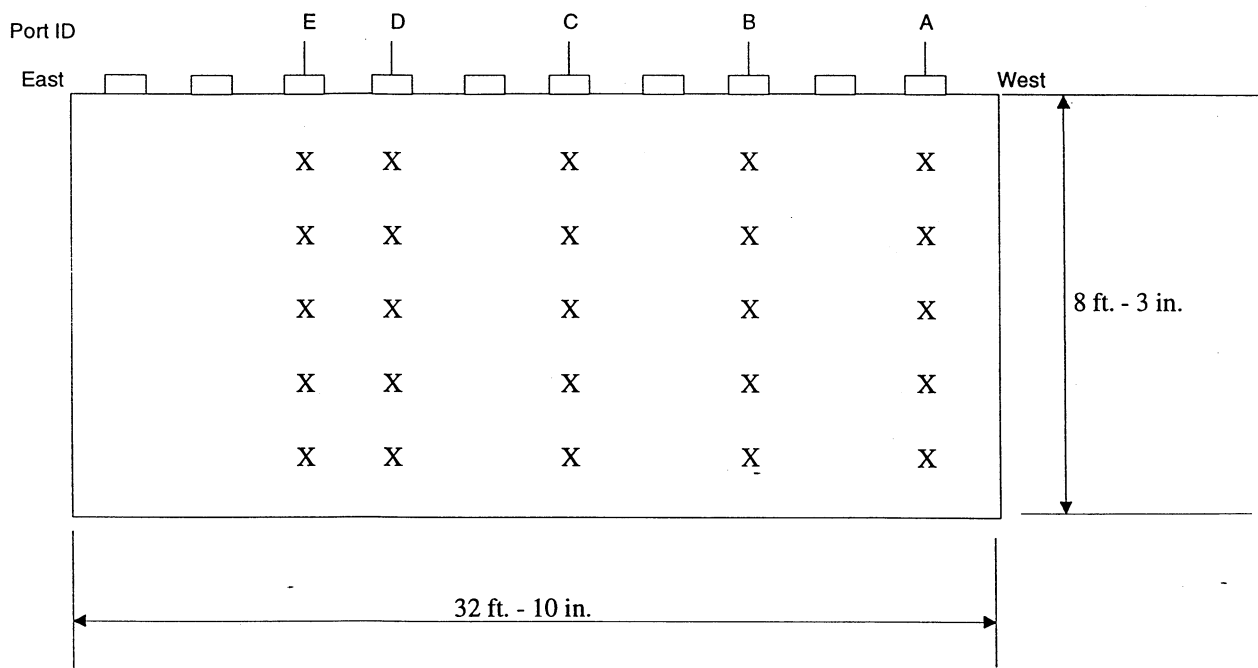
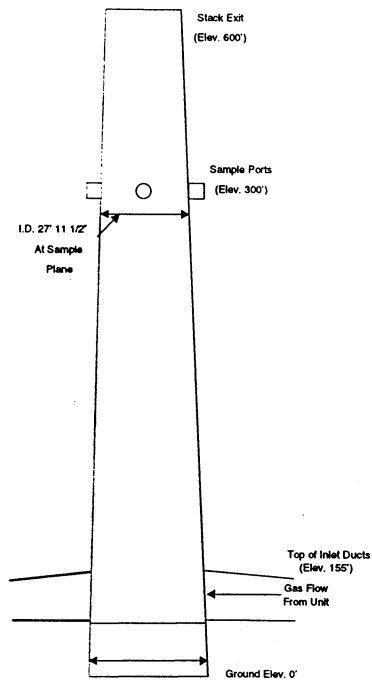
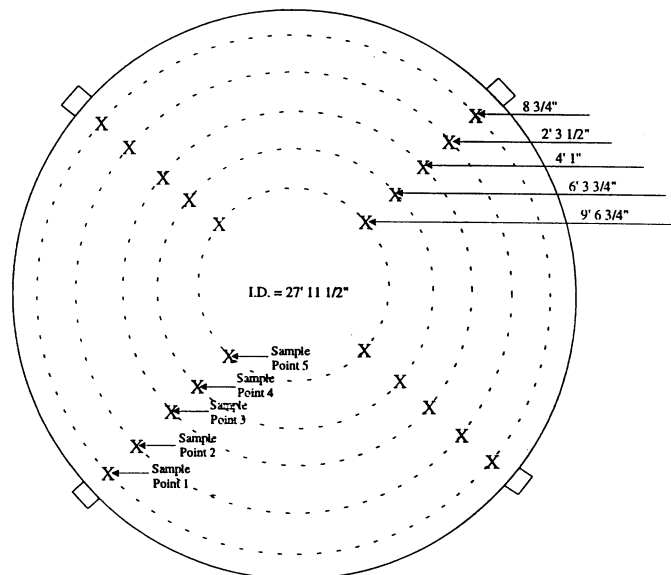


Figure 2-2b. Craig Unit 1 Inlet Sampling Location



a. Diagram of Stack



b. Cross-Section of Sample Location

Figure 2-3. Craig 1 Stack Sampling Location

This location meets the requirements of EPA Method 1. Cyclonic flow testing showed the flow angle to be less than 5 degrees at all sample points.

The flue gas at the stack was below the method specification of a minimum filtration temperature of 120°C. Therefore, heated filtration per Method 5 was used, with a minimum probe and filter temperature of 120°C.

2.3 Coal Sampling Location

Coal samples were collected from the silo just above the coal feeders to each individual mill. The lag time for coal to travel from the sample location to the boiler is approximately two minutes. One one-pint jar sample was collected from each mill during the first and last hour of each test run, and all samples were composited. Samples were collected by Mr. John Mihalich of Craig Station.

3

SUMMARY AND DISCUSSION OF TEST RESULTS

3.1 Objectives and Test Matrix

Objectives

The objective of the program is to collect the information and measurements required by the EPA Mercury ICR. Specific objectives are:

- Quantify speciated mercury emissions at the stack.
- Quantify speciated mercury concentrations in the flue gas at the scrubber inlet.
- Quantify fuel mercury and chlorine content during the stack and inlet tests.
- Provide the above information for use in developing boiler-, fuel-, and control device-specific mercury emission factors.

Test Matrix

The test matrix is presented in Table 3-1, and actual test times are shown in Table 3-2. Table 3-1 includes a list of test methods used. In addition to speciated mercury, the flue gas measurements included moisture, stack gas flow, and O₂/CO₂.

3.2 Field Test Changes and Problems

Sample Location at Inlet

As noted in Section 2.1 it was not possible to access the west duct inlet ports due to overhead obstructions, so only the east inlet duct was sampled. Sampling only one inlet duct is consistent with ICR sampling guidelines and is not believed to have any impact on the results, especially since no particulate phase mercury was measured during any of the inlet tests.

Sample Times at Inlet

Sample times at the inlet were adjusted because of the switch from two ducts to one duct, as follows:

Table 3-1. Test Matrix for Mercury ICR Tests at Craig Unit 1

Sampling Location	No. of Runs	Species Measured	Sampling Method	Sample Run Time	Analytical Method	Analytical Laboratory
Stack	3	Speciated Hg	Ontario Hydro	120 min	Ontario Hydro	Philip Services
Stack	3	Moisture	EPA 4	Concurrent	Gravimetric	FERCo
Stack	3	Gas Flow	EPA 1/2	Concurrent	Pitot Traverse	FERCo
Stack	3	O ₂	Batch Sample	Concurrent	Portable O ₂	FERCo
Stack	3	CO ₂	N/A	Concurrent	Plant CEMS	FERCo
Inlet	3	Speciated Hg	Ontario Hydro	125 min	Ontario Hydro	Philip Services
Inlet	3	Moisture	EPA 4	Concurrent	Gravimetric	FERCo
Inlet	3	Gas Flow	EPA 1/2	Concurrent	Pitot Traverse	FERCo
Inlet	3	O ₂	Batch Sample	Concurrent	Portable O ₂	FERCo
Inlet	3	CO ₂	N/A	Concurrent	Dilution calc	FERCo
Coal Feeders	3	Cl in coal	Modified ASTM D2234	1 grab sample per coal feeder per run	EPA SW 846: 5050/9056 (Cl)	Philip
Coal Feeders	3	HHV, Ash, S, Moisture	Modified ASTM D2234	1 grab sample per coal feeder per run	ASTM D514290	CTE
Coal Feeders	3	Mercury	Modified ASTM D2234	1 grab sample per coal feeder per run	Modified EPA 7371/1631	Frontier Geoscience

Table 3-2. Craig Unit 1 Sampling Times

Run No.	2	3	4
Date, 1999	28-Sep	28-Sep	29-Sep
Inlet Tests			
Start time	0824	1230	0820
Stop time	1038	1443	1044
Total sample time, min	125	125	125
Stack Tests			
Start time	0832	1230	0820
Stop time	1148	1512	1126
Total sample time, min	120	120	120
Notes:			
1. Gas flow, moisture, O ₂ were concurrent with mercury tests.			
2. Coal samples were collected during the first and last hour of each run.			

Original plan: 2 ducts x 5 ports x 5 points x 3 minutes/point = 150 minutes

Modified traverse: 1 duct x 5 ports x 5 points x 5 minutes/point = 125 minutes

Stack Sample Time

The stack sample time was reduced from 150 minutes (7 ½ minutes/point) to 120 minutes (6 minutes/point) to more closely coincide with the modified inlet sample time.

Inlet Sample Temperature

Due to low ambient temperatures, the average duct gas temperature for Run 3-Inlet was 244°F, which is below the minimum temperature of 120°C (248°F) specified for use of in-stack filtration. Following a conversation with Dennis Laudal of UNDEERC, it was determined that this discrepancy would have no impact on the results since the temperature was not low enough to cause either water or H₂SO₄ condensation in the flue gas on this unit.

Coal Mercury Analysis – Change Lab and Method

The test plan called for coal mercury analysis to be performed by Philip Analytical, using EPA SW846. However, the results for all three samples came back as ND<0.04 ppm, the stated detection limit for SW846.

In order to achieve lower detection limits, splits of the samples were sent to Frontier Geosciences for analysis by cold vapor atomic fluorescence (modified EPA 1631), following digestion by cold aqua regia (modified EPA 7371). These results provided detectable levels of mercury below 0.04 ppm, and are used as the reported coal mercury values.

Holding Time

Due to scheduling problems in the laboratory, the samples were analyzed 50 to 54 days after sampling. The Ontario Hydro Method specifies 45 days.

This discrepancy is not considered to have any impact on the results. Dennis Laudal of the University of North Dakota (the author of the Ontario Hydro Method) indicates that they have performed stability studies showing that samples are stable for at least 3 months.

3.3 Presentation of Results

The test results are presented in the following tables and figure:

- Table 3-3. Sample gas conditions.

Table 3-3. Craig Unit 1 Sample Gas Conditions

	Run 1	Run 2	Run 3	Average
Test Date	28-Sep	28-Sep	29-Sep	
Inlet Gas Properties				
Temperature, F	249	255	244	249
Gas flow for both ducts, dscfm	1,037,147	1,016,841	1,080,216	1,044,384
Comparison gas flows, dscfm				
Pitot traverse (x 2)	1,084,381	1,103,640	1,129,904	1,105,975
Calculated from fuel input and O ₂	1,061,385	1,094,847	1,099,531	1,085,254
Calculated from fuel input and CO ₂	986,334	988,235	1,078,839	1,017,803
O ₂ , %	7.32	7.24	7.69	7.42
CO ₂ , %	12.87	13.33	11.86	12.68
H ₂ O, %	8.43	8.33	7.98	8.25
Stack Gas Properties				
Temperature, F	148	147	136	144
Gas flow, dscfm (corrected pitot traverse)	1,025,070	1,007,255	1,040,062	1,024,129
Comparison gas flow, dscfm				
Calculated from fuel input and O ₂	1,049,026	1,084,525	1,058,659	1,064,070
Calculated from fuel input and CO ₂	974,849	978,918	1,038,736	997,501
Stack CEMS	972,579	960,956	984,031	972,522
O ₂ , %	7.16	7.11	7.18	7.15
CO ₂ , %	13.02	13.45	12.31	12.93
H ₂ O, %	10.91	13.04	11.48	11.81

- Table 3-4. Mercury concentration and speciation results.
- Table 3-5. Mercury removal across scrubber module and across scrubber system by species (note module and system removal are different due to scrubber reheat bypass).
- Figure 3-1: Mercury speciation across scrubber system.

Results are calculated as $\mu\text{g}/\text{sm}^3$ (at a reference temperature of 68°F), and normalized for dilution by converting to a $\text{lb}/10^{12}$ Btu basis. This method allows direct comparison of inlet and stack results without incorporating uncertainties involved in gas flow measurement.

Table 3-4. Craig Unit 1 Mercury Speciation Results

	Run 1	Run 2	Run 3	Average
Test Date	28-Sep	28-Sep	29-Sep	
Inlet Mercury Speciation				
Particulate mercury				
ug/dscm	ND<0.06	ND<0.06	ND<0.06	ND<0.06
lb/10 ¹² Btu	ND<0.06	ND<0.06	ND<0.06	ND<0.06
% of total Hg	0%	0%	0%	0%
Oxidized mercury				
ug/dscm	0.25	0.22	0.12	0.20
lb/10 ¹² Btu	0.24	0.21	0.11	0.19
% of total Hg	8%	10%	7%	9%
Elemental mercury				
ug/dscm	2.74	1.93	1.47	2.05
lb/10 ¹² Btu	2.57	1.79	1.42	1.93
% of total Hg	92%	90%	93%	91%
Total mercury				
ug/dscm	3.00	2.15	1.59	2.24
lb/10 ¹² Btu	2.81	2.00	1.53	2.11
Stack Mercury Speciation				
Particulate mercury				
ug/dscm	ND<0.007	ND<0.006	0.009	ND<0.007
lb/10 ¹² Btu	ND<0.006	ND<0.006	0.008	ND<0.006
% of total Hg	0%	0%	1%	0%
Oxidized mercury				
ug/dscm	0.097	0.083	0.072	0.084
lb/10 ¹² Btu	0.090	0.077	0.067	0.078
% of total Hg	6%	5%	4%	5%
Elemental mercury				
ug/dscm	1.64	1.61	1.56	1.60
lb/10 ¹² Btu	1.52	1.49	1.44	1.48
% of total Hg	94%	95%	95%	95%
Total mercury				
ug/dscm	1.73	1.69	1.64	1.69
lb/10 ¹² Btu	1.61	1.56	1.52	1.56
Coal Analysis				
Mercury, ppm dry	0.022	0.025	0.021	0.023
Mercury, lb/10 ¹² Btu	1.83	2.03	1.69	1.85
Chlorine, ppm dry	400	200	200	267
Moisture, %	15.84	14.81	18.08	16.2
Sulfur, % dry	0.52	0.52	0.58	0.54
Ash, % dry	8.02	8.17	6.37	7.52
HHV, Btu/lb as fired	10,370	10,604	10,200	10,391
Coal flow, lb/hr as fired	408,000	414,000	418,000	413,333
Total Mercury Mass Rates				
lb/hr input in coal	0.0077	0.0089	0.0072	0.0080
lb/hr at scrubber inlet	0.0116	0.0082	0.0064	0.0087
lb/hr emitted	0.0066	0.0064	0.0063	0.0064

Table 3-5. Craig Unit 1 Mercury Removal Efficiency

Run No.	1	2	3	Average
Date, 1999	28-Sep	28-Sep	29-Sep	
Estimated scrubber bypass, %	26	21	16	21
Total mercury				
Inlet, lb/10 ¹² Btu	2.81	2.00	1.53	2.11
Outlet, lb/10 ¹² Btu*	1.18	1.45	1.52	1.38
Stack, lb/10 ¹² Btu	1.61	1.56	1.52	1.56
System removal efficiency, %	42.8%	21.8%	0.7%	26.1%
Scrubber removal efficiency, %*	58.0%	27.5%	0.8%	34.6%
Particulate mercury				
Inlet, lb/10 ¹² Btu	ND<0.06	ND<0.06	ND<0.06	ND<0.06
Outlet, lb/10 ¹² Btu*	ND<0.06	ND<0.06	---	ND<0.06
Stack, lb/10 ¹² Btu	ND<0.006	ND<0.006	0.01	ND<0.007
System removal efficiency, %	N/A	N/A	N/A	N/A
Scrubber removal efficiency, %*	N/A	N/A	N/A	N/A
Oxidized mercury				
Inlet, lb/10 ¹² Btu	0.24	0.21	0.11	0.19
Outlet, lb/10 ¹² Btu*	0.04	0.04	0.06	0.05
Stack, lb/10 ¹² Btu	0.09	0.08	0.07	0.08
System removal efficiency, %	62%	63%	42%	58%
Scrubber removal efficiency, %*	84%	79%	50%	75%
Elemental mercury				
Inlet, lb/10 ¹² Btu	2.57	1.79	1.42	1.93
Outlet, lb/10 ¹² Btu*	1.14	1.41	1.45	1.33
Stack, lb/10 ¹² Btu	1.52	1.49	1.44	1.48
System removal efficiency, %	41%	17%	-2%	23%
Scrubber removal efficiency, %*	56%	22%	-2%	31%

*Notes-Outlet concentrations and scrubber removal efficiency are calculated values.

“Scrubber removal efficiency” is the calculated removal across a scrubber module, with no bypass.

“System removal efficiency” is the measured removal across the scrubber system, including bypass.

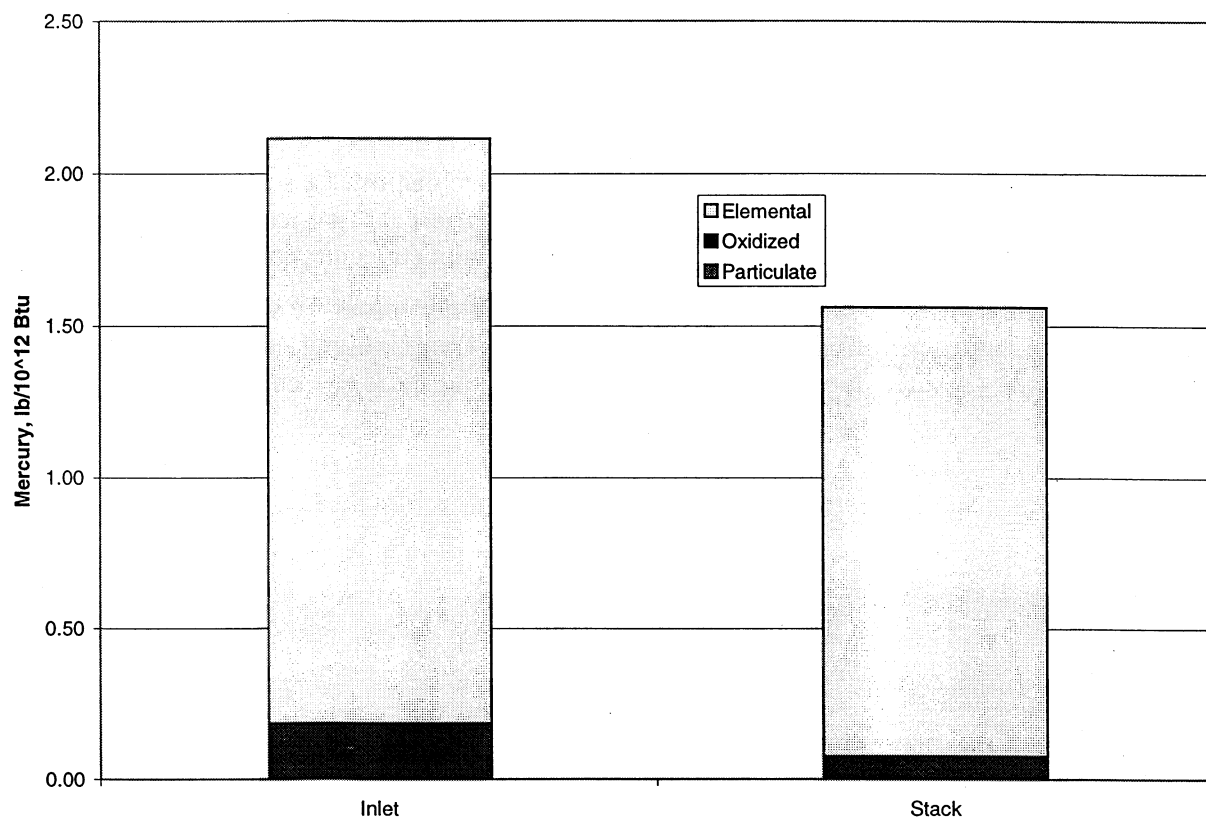


Figure 3-1. Mercury Speciation Across Craig Unit 1 Scrubber System

Major observations that can be made from the results are:

1. Mercury is primarily in the elemental phase at both the inlet (91% of total mercury) and at the stack (95% of total mercury). Oxidized mercury was 9% of the total at the inlet and 5% of the total at the stack. There was no measurable particulate mercury at either the inlet or stack.
2. Mercury levels in the coal were 0.021 to 0.025 ppm, with an average input rate of 0.0080 lb/hr. The mercury mass rate at the inlet was 0.0087 lb/hr, or 9% higher than the fuel input. The difference of 15% is considered to be within the uncertainties of the measurement methods.
3. Oxidized mercury was removed with 58% efficiency across the scrubber system (including bypass) and 75% efficiency across the modules. There is significant data scatter in removal efficiency results, primarily due to variability in inlet concentrations.
4. Elemental mercury was removed with 23% efficiency across the scrubber system (including bypass) and 31% efficiency across the modules. There is significant data scatter in removal efficiency results, due to variability in both inlet and stack concentrations.

4

SAMPLING AND ANALYTICAL PROCEDURES

4.1 Test Methods

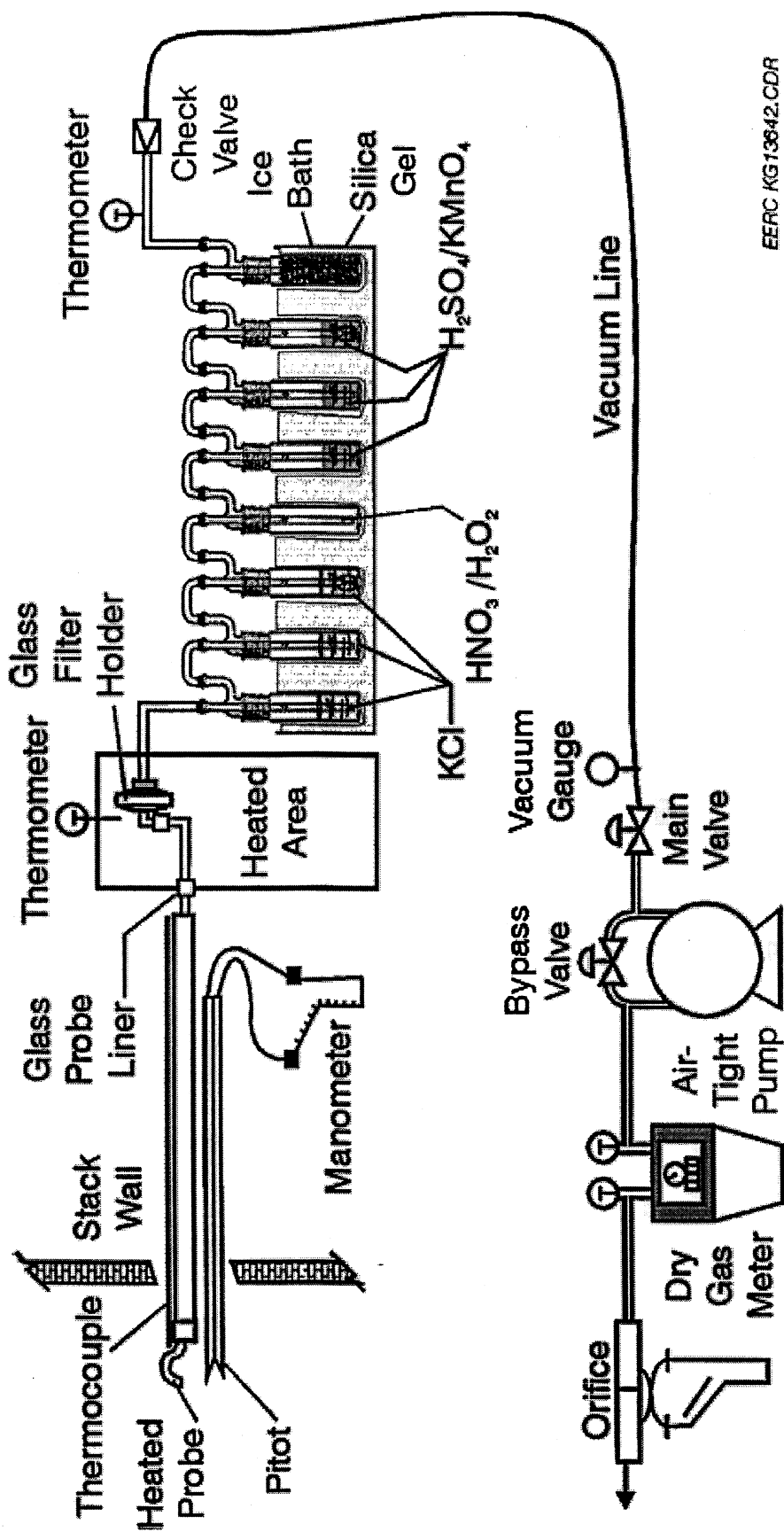
This section contains a summary of the sampling and analytical procedures used to conduct the mercury speciation required in EPA's ICR titled, "Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)" dated April 8, 1999. The full text of the method was presented as Appendix A of the Test Plan.

Subsequent to submittal of the Test Plan, additional drafts of the Ontario Hydro Method were published. Wherever possible, the new features of these drafts were incorporated into the program.

Speciated mercury samples were collected in three test runs at the inlet and outlet of the control device. The inlet and outlet sampling were concurrent. A field blank was collected at each test location on September 27, the set up day. The field blank consisted of assembling a sample train, transporting it to the sample location, conducting a leak check, letting the train sit for two to three hours, and then recovering the train as if it were a sample.

EPA methods to determine flue gas flow rate were used. EPA Reference Method 5 and 17 requirements for isokinetic sampling were followed. Each impinger was weighed before and after sampling to determine flue gas moisture content.

Figure 4-1 presents a schematic of the mercury speciation sample train, Table 4-1 presents a list of sample train components for the Method 17 configuration, and Table 4-2 presents a list of sample train components for the Method 5 configuration. The sampling train was set up with in-stack filtration (EPA Method 17 configuration) for the inlet location and external heated filtration (EPA Method 5 configuration) for the stack location.



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Figure 4-1. Schematic of the Mercury Speciation Sample Train
(Method 5 option as used at the stack is shown; Method 17 in-stack filtration was used for the Inlet on Craig 1)

Table 4-1. Sample Train Components - Method 17 Configuration

Component	Details
Nozzle	Glass.
Filter	Quartz thimble, in glass thimble holder.
Probe	Teflon, heated to minimum 120 C.
Connector line	Heated teflon line used to connect from probe to impingers. Heated to minimum 120 C.
Impingers 1, 2	1 mol/l KCl solution; modified Smith Greenburg (SG) impinger.
Impinger 3	1 mol/l KCl solution; standard Smith Greenburg impinger.
Impinger 4	5% nitric acid/10% hydrogen peroxide; modified SG impinger.
Impingers 5, 6	4% potassium permanganate/10% sulfuric acid; modified SG impinger.
Impinger 7	4% potassium permanganate/10% sulfuric acid; standard SG impinger.
Impinger 8	Silica gel; modified Smith Greenburg Impinger

Table 4-2. Sample Train Components - Method 5 Configuration

Component	Details
Nozzle	Glass
Probe	Glass, heated to minimum 120 C.
Filter	Quartz, in glass holder, heated to minimum 120 C.
Filter support	Teflon.
Connector line	Heated teflon line used to connect from filter outlet to impingers. Heated to minimum 120 C.
Impingers 1, 2	1 mol/l KCl solution; modified Smith Greenburg (SG) impinger.
Impinger 3	1 mol/l KCl solution; standard Smith Greenburg impinger.
Impinger 4	5% nitric acid/10% hydrogen peroxide; modified SG impinger.
Impingers 5, 6	4% potassium permanganate/10% sulfuric acid; modified SG impinger.
Impinger 7	4% potassium permanganate/10% sulfuric acid; standard SG impinger.
Impinger 8	Silica gel; modified Smith Greenburg Impinger

Sample was withdrawn from the flue gas stream isokinetically through the filtration system, which was followed by a series of impingers in an ice bath. Particulate-bound mercury was collected on the front half and filter; oxidized mercury was collected in impingers containing 1 N potassium chloride solution; and elemental mercury was collected in one impinger containing a 5% nitric acid and 10% peroxide solution, and in three impingers containing a solution of 10% sulfuric acid and 4% potassium permanganate. An impinger containing silica gel collected any remaining moisture.

The filter media was quartz fiber filters. At the inlet, a quartz thimble in a glass holder was used. At the stack, a 105 mm quartz filter in a glass filter holder was used. At the inlet the probe included a heated teflon line; at the stack a heated glass probe was used. An additional heated teflon line was used to transport the flue gas from the end of the probe to the inlet of the first impinger. Both the probe and the line were heated to maintain a minimum gas temperature of 248°F.

A two hour sampling time was used at the stack, with a target sample volume of 1 to 2.5 standard cubic meters. At the inlet, a sample time of 125 minutes was used.

Sample Recovery

Figure 4-2 is a schematic of the sample recovery procedure for the impinger train. The samples were recovered into precleaned glass bottles with vented teflon lined lids for shipment to the laboratory. The following sample fractions were recovered (specific rinse solutions are contained in the method):

1. The sample filter;
2. The front half rinse (includes all surfaces upstream of the filter)
3. Impinger 1 through 3 (KCl impingers) and rinses;
4. Impinger 4 (HNO₃/H₂O₂ impinger) and rinses;
5. Impingers 5 through 7 (KMnO₄/H₂SO₄ impingers) and rinses;
6. Impinger 8 (silica gel impinger). Note this sample is weighed for moisture determination and is not included in the mercury analysis.

Sample Digestion and Analysis

The sample fractions were digested and analyzed as specified in the method and summarized below:

Ash Sample (Containers 1 and 2)

If the particulate catch is greater than 1 gram (as would be the case at most particulate control device inlet locations), an aliquot of the particulate collected on the filter is digested by microwave digestion.

KCl Impingers (Container 3)

The impingers are digested using H_2SO_4 , HNO_3 , and KMnO_4 solutions as specified in the method.

KNO_3 - H_2O_2 Impinger (Container 4)

The impinger solution is digested using HCl and KMnO_4 solutions as specified in the method.

H_2SO_4 - KMnO_4 Impingers (Container 5)

The impinger solution is digested using hydroxylamine sulfate as specified in the method.

Analysis

Each digested fraction is analyzed in duplicate for total mercury by cold vapor atomic absorption (CVAAS). CVAAS is a method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbency is measured as a function of mercury concentration. A soda-lime trap and a magnesium perchlorate trap must be used to precondition the gas before it enters the absorption cell.

1. Rinse filter holder and connector with 0.1N HNO_3 .
2. Add $\text{H}_2\text{SO}_4/\text{KMnO}_4$ to each impinger bottle until purple color remains.
3. Rinse with 0.1N HNO_3 .
4. Rinse with 8N HCl if brown residue remains.
5. Final rinse with 0.1N HNO_3 .

Rinse Bottles Sparingly with

- 0.1N HNO_3
- 8N HCl
- 0.1N HNO_3

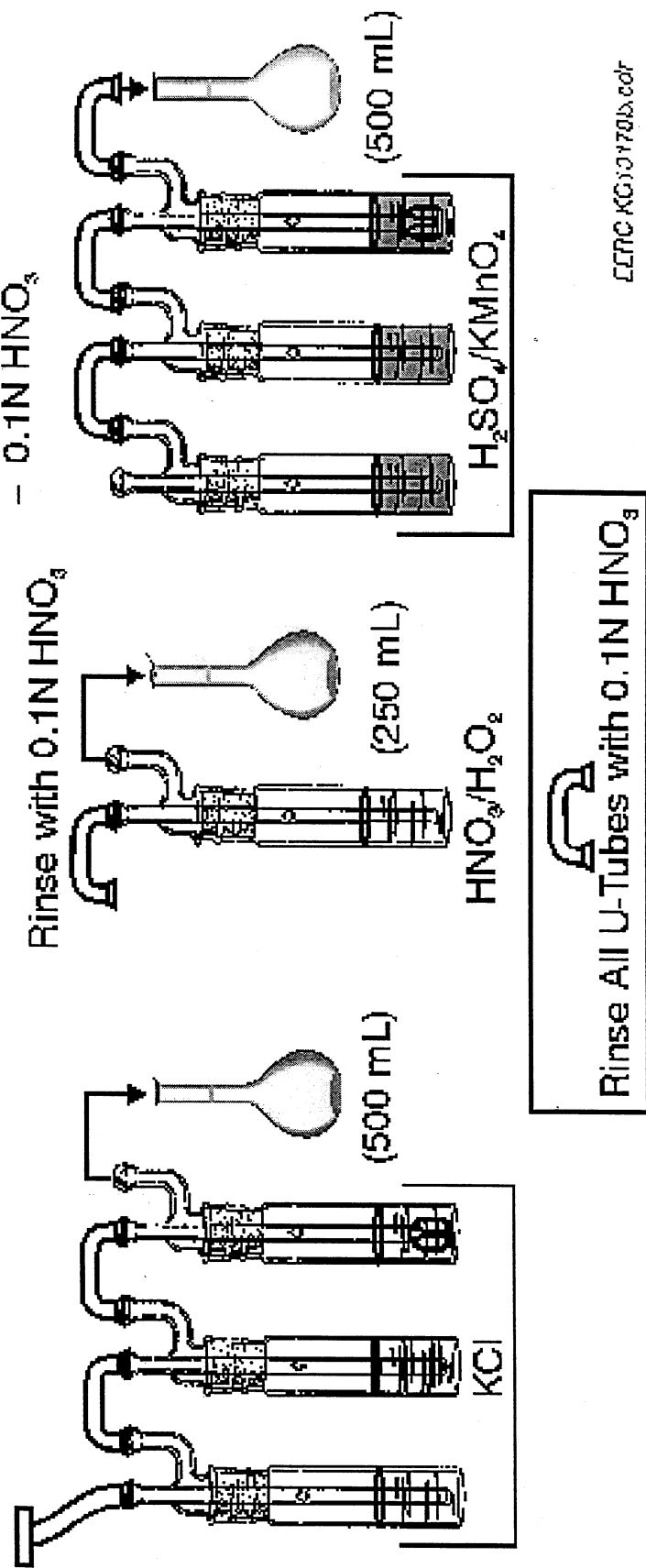


Figure 4-2. Sample Recovery Scheme for the Mercury Sampling Train

Handling of Non Detects

This section addresses how data was handled in cases where no mercury was detected in an analytical fraction.

A single analytical fraction representing a subset of a mercury species is not detected. When more than one sample component is analyzed to determine a mercury species and one fraction is not detected, it is counted as zero. This occurred on several samples for elemental mercury, which is the sum of the mercury collected in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger and the $\text{H}_2\text{SO}_4/\text{KMnO}_4$ impingers. For example, on Test 3-Stack the H_2O_2 fraction was $\text{ND}<0.25\ \mu\text{g}$ and the KMnO_4 fraction was $2.6\ \mu\text{g}$. Elemental mercury was reported as $2.6\ \mu\text{g}$.

Mercury is detected on one or two of three runs. If mercury is detected on one or two of three runs, average mercury is calculated as the average of the detected value(s) and half of the detection limits for the non detect(s). However, if this average is below the detection limit, the average is reported as not detected.

For example, the particulate mercury results for the three stack tests (in units of $\text{lb}/10^{12}\ \text{Btu}$) are $\text{ND}<0.006$, $\text{ND}<0.006$, and 0.008 . The average using half the detection limit is $(0.003 + 0.003 + 0.008)/3$, or 0.005 . Since this value is below the detection limit of 0.006 , the results are reported as $\text{ND}<0.006$.

No mercury is detected for a species on all three test runs. When all three test runs show no detectable levels of mercury for a mercury species, that mercury species is reported as not detected at less than highest detection limit. For example, the results for the three inlet particulate mercury runs were all $\text{ND}<0.06\ \text{lb}/10^{12}\ \text{Btu}$. The average is reported as $\text{ND}<0.06\ \text{lb}/10^{12}\ \text{Btu}$.

In summing up individual species to determine total mercury, a value of zero is used for non-detected species. For example, the average inlet mercury values (in $\text{lb}/10^{12}\ \text{Btu}$) were $\text{ND}<0.06$ for particulate mercury, 0.19 for oxidized mercury, and 1.93 for elemental mercury. Total mercury is reported as $0.19 + 1.93$, or 2.12 .

In calculating the percentage of mercury in each two species, a value of zero is used for the non-detected species. For the example listed in the preceding paragraph, the results are reported as 0% particulate mercury, 9% oxidized mercury, and 91% elemental mercury.

Auxiliary Flue Gas Measurements

Auxiliary flue gas measurements performed were flue gas flow rate per EPA Methods 1 and 2 (pitot traverse), O_2 by portable O_2 analyzer (as described below), and H_2O by EPA Method 4 (condensation/gravimetric analysis). These measurements were collected as integral parts of all mercury speciation test runs at both the inlet and stack locations.

Stack Flow Bias Correction

Previous studies at Craig have shown that S-type pitot probe measurements produce a false positive bias due to non axial flow, even though the degree of non axial flow is within the tolerance of Methods 5 and 17 for isokinetic sampling.

To correct for this bias, measured S-type pitot stack flow rates were multiplied by a correction factor to determine stack flow rates. The correction factors were obtained by comparison of 3-dimensional flow test results per Method 2F and S-type pitot measurements per Method 2 from the annual RATA program conducted prior to the ICR tests. The stack flow correction factor applied to the Craig 1 S-type pitot traverses was 0.959.

Corrected stack flow results are used to report stack flow rate, and to calculate mercury emissions in lb/hr.

The gas velocity measurements were not corrected when used to establish isokinetic gas sampling rates, since the flow uncertainty is within normal Method 5 tolerances.

Inlet Flow Determination

There will typically be higher uncertainties in gas flow measurements at the inlet location relative to the stack location due to non axial flow. To calculate mercury levels in terms of lb/hr at the inlet, the outlet flow, corrected for dilution using O₂ measurements, was used for inlet values. This allows direct comparison of inlet and outlet mercury measurements without incorporating added uncertainty from the gas flow measurements.

Comparative Flow Rate Calculations

As a QA indicator, additional flow rate determinations were done. At both locations, exhaust gas flow was calculated based on boiler fuel input and both oxygen (F_d) and carbon (F_c) F factors. At the stack, the plant CEMS stack flow rate is presented. At the inlet the pitot traverse results, multiplied by two since only one of two ducts was tested, are presented in Table 3-3.

Alternate Methodology for O₂/CO₂ Determination

As an alternate to conventional Orsat analysis, the following procedure was used for determination of O₂ and CO₂ content.

O₂ determination. O₂ was measured by a portable O₂ analyzer using an electrochemical cell. The gas sample for the portable analyzer was drawn through a tube inserted in the exit gas of the sample gas meter. This provides direct analysis of the gas sampled for the mercury test. Care was taken that the O₂ sample tube was not inserted so far that it interfered with the meter orifice pressure differential reading. Calibration procedures for the portable analyzer included:

1. At the beginning of the test day, the instrument was calibrated on ambient air. As-found readings were then taken using zero gas and an EPA Protocol 1 mid scale O₂ calibration gas (40 to 60% of the span used to collect readings). If these as found readings were within 2% of span, the data was acceptable. If the readings were outside of these ranges, the O₂ cell was replaced, the instrument was repaired, or an alternate instrument was used.
2. During testing, the calibration of the instrument was checked on ambient air every three or four sample points. If the as-read value on air had drifted more than 0.2% O₂ (0.8% of scale), the instrument was recalibrated.
3. At the end of the test day, the calibration error step described in Step 1 above was repeated.

CO₂ determination. CO₂ is used for molecular weight determination. At the stack, CO₂ readings were taken from the plant CEMS. Since the CEMS readings are on a wet basis, they were converted to a dry basis using the moisture content measured by the mercury train.

At the inlet, the CO₂ was calculated via dilution calculations from the inlet O₂, the stack O₂, and the stack CO₂.

Determination of Scrubber Mercury Removal Efficiency

The scrubber system on Craig Unit 1 includes bypass of a portion of the flue gas for reheat purposes. Therefore direct comparison of inlet and stack mercury levels provides removal efficiency information for the Craig Unit 1 system, but does not provide direct measurement of the removal efficiency of the scrubber modules themselves. Scrubber module removal efficiency is of interest, since these results will be used to develop emission factors for a variety of units that may or may not have bypass systems.

In general, control device removal efficiency is calculated according to Equation 1 below:

$$(1) \quad E = 1 - C_{\text{out}}/C_{\text{in}}$$

Where,

E = removal efficiency

C_{out} = Concentration at scrubber outlet

C_{in} = Concentration at scrubber inlet

It is important that the inlet and outlet values be corrected for air leakage to provide results on a consistent basis. For this program, the correction was achieved by calculating mercury concentration in units of lb/10¹² Btu. Mass emission rates were not used because of the relatively high uncertainties associated with gas flow measurement.

The scrubber outlet concentration can be calculated from the inlet and stack test results. The measured stack concentration can be expressed as shown in Equation 2:

$$(2) \quad C_{\text{stack}} = (\text{BF} \times C_{\text{in}}) + ((1-\text{BF}) \times C_{\text{out}})$$

Where,

C_{stack} = Measured concentration at stack

BF = fraction of gas bypassed, unitless. A discussion of bypass flow determination is presented below.

Solving for C_{out} in Equation 2 yields Equation 3:

$$(3) \quad C_{\text{out}} = (C_{\text{stack}} - (\text{BF} \times C_{\text{in}})) / (1-\text{BF})$$

The outlet concentration derived from Equation 3 can then be used to determine control device efficiency using Equation 1.

Determination of Bypass Fraction

As outlined in the Test Plan Addendum, it was planned to calculate the bypass fraction from measurements of gas temperature and moisture at the inlet, outlet, and stack using mass and heat balance equations. However, it was learned on site during the tests that there were no temperature measurements available at the outlets of the scrubber modules. Therefore, a modified estimation approach was used:

1. An outlet temperature was estimated, and the bypass fraction was calculated using this outlet temperature and heat balance equations.
2. The saturation moisture corresponding to the estimated outlet temperature was calculated (assuming no significant quantity of liquid passes the demisters). The bypass fraction was calculated using this moisture and mass balance equations.
3. The bypass fractions calculated in steps 1 and 2 were compared. If they differed by more than 2%, steps 1 and 2 were repeated with a new assumed temperature. If they were within 2%, the average value was taken as the bypass fraction.

This process provided bypass estimates of 26% for Run 1, 21% for Run 2, and 16% for Run 3, with an average of 21%. The uncertainty in the bypass calculations is estimated at 5%. The average value of 21% is consistent with the design range of 20 to 23%.

4.2 Process Data

Process data was collected on computer logs set up by station personnel. Data collected included key boiler, scrubber, and ESP operating parameters, and all CEMS data.

Prior to and during each test, unit operation was assessed by station personnel to assure that operating conditions were within project target ranges.

5

INTERNAL QA/QC ACTIVITIES

5.1 QA/QC Problems

There were no sampling related QA/QC problems. All KMnO_4 impingers were purple at the conclusion of each test.

5.2 QA Audits and Data Quality Objectives

QA audit samples were analyzed as specified in the Ontario Hydro Method and listed in Table 5-1. Data quality objectives are listed in Table 5-2. Table 5-3 presents audit results and compares data quality results with data quality objectives. Table 5-4 presents individual mercury fraction mass measurements, along with field blank results.

All data quality objectives were met, with the following exceptions:

1. The target of the results, all runs being within 35% of the mean, was not met for one of the three runs on oxidized mercury at the inlet. This does not necessarily indicate a problem, just that there was more data scatter than hoped for. The cause could be either process, sampling, or analytical related.
2. The inlet filter field blank had 0.082 μg of mercury, compared to $\text{ND} < 0.080$ for the three samples. This is not considered significant.
3. The inlet field blank KCl level was 59% of the average level measured for the three tests, exceeding the target of 30%. Note that both the field blank and sample mercury values are low (0.16 and 0.27 $\mu\text{g}/\text{sample}$, respectively)

The cause for this is unknown. Since the reagent blanks had no mercury, contamination of the field blank was most likely from sample handling. Contamination from sample handling tends to be random, so no speculation can be made on the potential impact of this field blank result on overall test results.

Table 5-1. Audit Samples for Ontario Hydro Mercury Speciation

Audit Sample	Acceptance Criteria and Frequency	Reference
Known reagent spike	Every 10 samples.	Ontario Hydro Section 13.4.1
Certified reference ash	One per program.	Ontario Hydro Section 13.4.1

Table 5-2. Data Quality Objectives for Flue Gas Mercury Analyses

<i>Measure</i>	<i>Objective</i>	<i>Approach</i>
Accuracy	$\leq 10\%$ of sample value or $\leq 10\times$ instrument detection limit	Reagent blanks-analyze one blank per batch of each reagent
Accuracy	Field blank $\leq 30\%$ of sample value, or no greater than reagent blank; whichever is higher	Collect and analyze one field blank at inlet and one at outlet; criteria evaluated for each mercury species
Accuracy	$\pm 10\%$ of nominal value	One known reagent spike every ten samples
Precision, lab analysis	$\leq 10\%$ RPD	All laboratory samples analyzed in duplicate, every 10th sample analyzed in triplicate
Completeness	$\geq 95\%$	Failed or incomplete tests to be repeated, if possible and practical

Table 5-3. Results Evaluation and Verification Checklist

Measure	Objective	Result
<i>Unit Operation</i>		
Unit operating conditions	No unusual conditions	Steady, normal operation
Air pollution control device operation	No unusual conditions	Steady, normal operation
<i>Sample Train Information</i>		
Trains leak checked before/after each test	<0.02 cfm	All tests passed
Pitot probes leak checked	Zero leakage	All tests passed
Probe, line, and filter temperature maintained	Minimum 120 C	All tests passed
Sample rate isokinetics	90-110%	96-102% at inlet 92-104% at stack
Sample volume	1-2.5 std cubic meters	1.2-1.4 m ³ at inlet 1.5-1.7 m ³ at stack
Post-test color of permanganate impingers	Purple	All tests passed
<i>Results/lab QA</i>		
Flow rate for triplicate runs	All runs w/in 10% of mean (adjusted for load)	All flows w/in 2% of mean at inlet and stack.
Stack temperature for triplicate runs	All runs w/in 5% of mean	W/in 1% at inlet W/in 3% at stack
Total mercury for triplicate runs	All runs w/in 35% of mean	W/in 33% at inlet W/in 3% at stack
Particulate mercury	All runs w/in 35% of mean	Not detected at inlet W/in 20% at stack
Oxidized mercury	All runs w/in 35% of mean	One run 42% below mean at inlet, one run 26% above mean, and one run 11% above mean W/in 15% at stack
Elemental mercury	All runs w/in 35% of mean	W/in 33% at inlet W/in 3% at stack
Sample and blank spikes	w/in 10% of value	All tests passed
Field blanks	<30% of measured values	See Table 5-4

Table 5-4. Craig Unit 1 Sample Fraction Mercury Measurements

	Run 1	Run 2	Run 3	Average	Field blank	Field blank/ sample, %
Inlet, µg/sample						
Filter/probe wash (particulate Hg)	ND<0.080	ND<0.080	ND<0.080	ND<0.080	0.082	see note
KCl fraction (oxidized Hg)	0.33	0.31	0.17	0.27	0.16	59%
H ₂ O ₂ fraction (elemental Hg)	0.96	ND<0.25	ND<0.25	0.40	ND<0.25	ND
KMnO ₄ fraction (elemental Hg)	2.60	2.70	2.10	2.47	ND<0.030	ND
Stack, µg/sample						
Filter/probe wash (particulate Hg)	ND<0.010	ND<0.010	0.015	ND<0.010	ND<0.010	ND
KCl fraction (oxidized Hg)	0.15	0.14	0.12	0.14	ND<0.10	ND
H ₂ O ₂ fraction (elemental Hg)	ND<0.25	ND<0.25	ND<0.25	ND<0.25	ND<0.25	ND
KMnO ₄ fraction (elemental Hg)	2.50	2.70	2.60	2.60	ND<0.050	ND
Note: filter field blank was just above detection limit. Value is not considered significant.						

MERCURY SPECIATION STACK SAMPLING TEST REPORT: CRAIG STATION UNIT 3

January 2000

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1

INTRODUCTION

1.1 Summary of Test Program

Purpose of Test

The United States Environmental Protection Agency (EPA) has implemented an Information Collection Request (ICR) aimed at characterizing mercury emissions from coal-fired power plants in the United States. As part of this ICR, the operators of selected coal-fired boilers were required to collect and analyze flue gas samples for particulate, elemental, and oxidized mercury.

Tri-State Generation and Transmission's (Tri-State's) Craig Unit 3 was selected at random by the EPA to provide speciated mercury emissions data, which will then be used to develop emission factors for boilers in its class.

Measurements collected were speciated mercury emissions at the stack, speciated mercury concentrations at the inlet of the boiler's last air pollution control device (a dry lime scrubber), and fuel mercury, chlorine, moisture, sulfur, ash, and heating value.

Test Unit

The test unit is Craig 3. This unit is operated by Tri-State Generation and Transmission Association (Tri-State), and is located in Craig, Colorado. The unit was selected by the EPA as part of the following category:

- Fuel type: subbituminous
- SO₂ control type: dry scrubber
- Particulate control type: fabric filter

The unit is rated at 435 MW gross. Craig 3 is a Babcock & Wilcox opposed-fired boiler, with original equipment low-NO_x burners for NO_x control. It fires local low sulfur subbituminous coal from the Colowyo and Trapper mines. SO₂ emissions are controlled by a dry scrubber.

Test Measurements

The program included the following tests, with triplicate sets of measurements performed simultaneously at each test location:

- Particulate, oxidized, and elemental mercury emissions at the stack per the Ontario Hydro mercury speciation method.
- Particulate, oxidized, and elemental mercury concentrations at the two air preheater exit ducts. This location, referred to as the "inlet", is upstream of the inlet ducts to the individual dry scrubber modules.
- Mercury and chlorine content of representative coal samples collected from the coal feeders.
- Coal moisture, sulfur, ash, and heating content.

Responsible Organizations

Responsible organizations for this project are:

- Test site operator: Tri-State
- Program sponsor: Electric Power Research Institute (EPRI)
- Sampling team: Fossil Energy Research Corp. under contract to EPRI, with Delta Air Quality Services as a major subcontractor
- Sample analysis: Philip Analytical Services (flue gas mercury, coal chlorine), Commercial Testing and Engineering (coal HHV, S, ash, moisture), Frontier Geosciences (coal mercury)

Dates of Test

The test program was conducted on October 2-5, 1999. Daily activities included:

- October 2: set up and conducted field blanks.
- October 4: conducted Runs 1 and 2.
- October 5: conducted Run 3.

Document Description

This document is the test report for the Craig Unit 3 mercury ICR testing. It has been prepared in accordance with Emission Measurement Center Guideline Document GD-043, as required in the ICR.

The work described here is based on the Craig Unit 3 Test Plan (Report No. FERCo R675), the Craig Unit 3 Quality Assurance Plan (Report No. FERCo R698), and the Craig Unit 3 Test Plan Addendum (Report No. FERCo R722). These reports are available from Tri-State, the EPA or FERCo.

The Test Plan Addendum was prepared in response to initial EPA review of the Test Plan. The Test Plan Addendum was approved by Mr. William Grimley of the EPA. The QA Plan was

approved by Ms. Lara Autry of the EPA prior to testing. EPA comments on the draft QA Plan were incorporated into the final version of the QA Plan.

1.2 Key Personnel

Table 1-1 lists the test program organization and key individuals with responsibilities, phone numbers, and e-mail addresses. A program organizational chart is shown in Figure 1-1.

The program was jointly funded by Tri-State and EPRI. FERCo was under contract to EPRI. The Project Quality Assurance Officer was Greg Quartucy of FERCo, who reported directly to Larry Muzio, FERCo's Vice President. External QA activities were performed by Dennis Laudal of UNDEERC. Mr. Laudal reported directly to Paul Chu of EPRI. Both UNDEERC and FERCo are contractors to EPRI. The reporting function from Mr. Laudal to Mr. Chu is considered to be external to FERCo's project.

Ms. Garaas, Mr. McDannel, and Ms. Bell were all on-site for the testing. There were no observers from regulatory agencies.

Table 1-1. Test Program Organization and Responsibilities

Organization	Individual	Responsibility	Reports To	Phone Number	Fax Number	E-mail Address
Project Management and Oversight						
EPRI	Paul Chu	EPRI Project Manager	N/A	(650) 855-2812	(650) 855-2619	pchu@epri.com
FERCo	Lawrence Muzio	Vice President	N/A	(949) 859-4466	(949) 859-7916	lmuzio@ferco.com
FERCo	Greg Quartucy	QA Manager	Lawrence Muzio	(949) 859-4466	(949) 859-7916	gquartucy@ferco.com
Host Utility						
Tri-States	Ed Lasnik	Program Coordinator	N/A	(303) 452-6111	(303) 254-6013	edlasn@tristategt.org
Tri-States	Christina Garaas	On-site Coordinator	N/A	(303) 452-6111	(303) 254-6013	cgaraas@tristategt.org
FERCo/Delta Sampling Team						
FERCo	Mark McDannel	Program Manager	Paul Chu	(949) 859-4466	(949) 859-7916	mmcdannel@ferco.com
Delta	Arlene Bell	Project Chemist	Mark McDannel	(714) 279-6777	(714) 279-6781	deltaaqs@aol.com
Philip Environmental	Ron McLeod	Sample Analyses	Mark McDannel	(905) 332-8788	(905) 332-9169	rmcleod@philipinc.com
External QA/QC						
UNDEERC	Dennis Laudal	External QA/QC	Paul Chu	(701) 777-5138	(701) 777-5181	dlaudal@eerc.und.nodak.edu

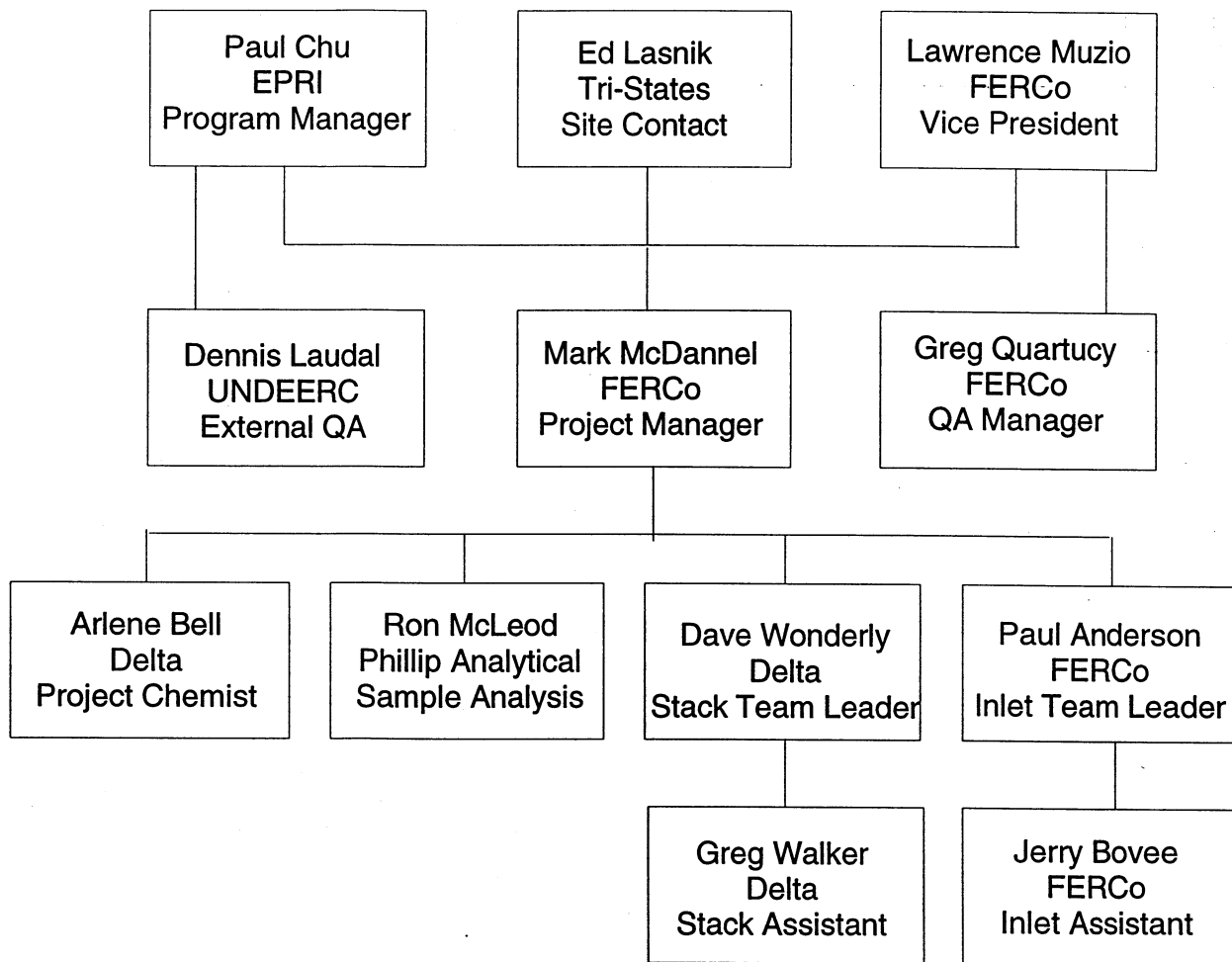


Figure 1-1. Project Organization Chart

2

PLANT AND SAMPLING LOCATION DESCRIPTIONS

2.1 Process and Control Equipment Description and Operation

Craig 3 is an opposed-fired Babcock & Wilcox boiler rated at 435 MW gross. Figure 2-1 shows a schematic of the boiler and pollution control equipment, including sample points.

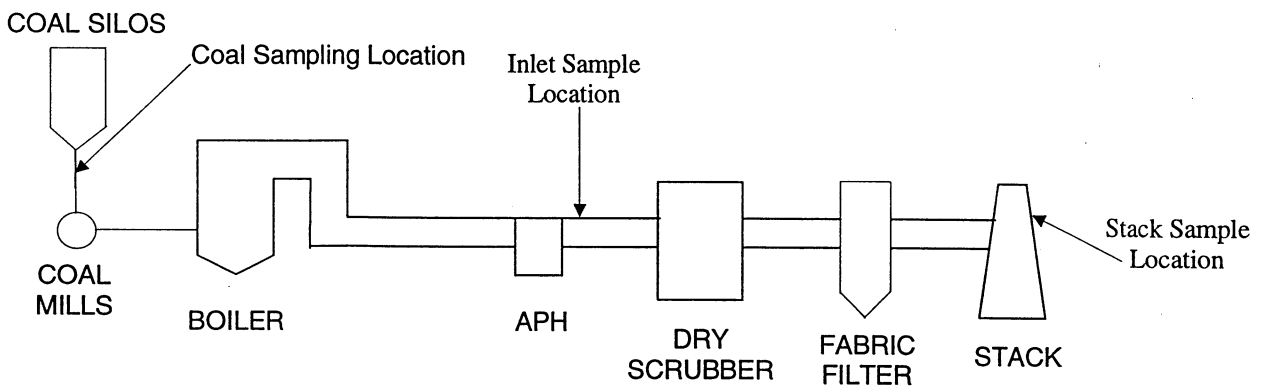


Figure 2-1. Craig Unit 3 Schematic

Key unit parameters include:

- Unit capacity: 435 MW gross
- Boiler type: Babcock & Wilcox, opposed-fired, balanced draft
- Fuel type: subbituminous, from Colowyo and Trapper mines
- SO₂ control: dry scrubber. A slurry of lime and recycled baghouse fly ash is used as the reagent. Typically, three of the four scrubber modules are in service. Steam reheat is used on the outlet gas to maintain a minimum stack temperature of 170°F. Scrubber bypass is also used for reheat if the steam reheat can not maintain 170°F. For these tests, no bypass was used.
- Particulate control: fabric filter baghouse, air cloth ratio 1.8:1 with all 24 compartments in service. 99.9% efficiency
- NO_x control: original equipment low NO_x burners

Fuel samples were collected at the coal feeders ahead of the boiler, inlet samples were collected at the inlet to the dry scrubber, and outlet samples were collected at the stack.

The sample gas at the inlet was approximately 280°F. At the stack, the gas temperature was approximately 180°F.

Unit operation during testing was at or near nominal full load, at steady state operation. Coal type, boiler operation, and control device operation were all within normal operating ranges. Three of the four scrubber modules were in service for the tests.

Table 2-1 presents a summary of unit operation during the tests. Additional detailed unit data is included in Appendix G.

Table 2-1. Summary of Craig Unit 3 Operation

Run No.	1	2	3
Date, 1999	4-Oct	4-Oct	5-Oct
Start time	0921	1336	0830
Stop time	1233	1636	1142
Unit load, MW net	409	408	410
Coal mills in service	A, C, D, E	A, C, D, E	A, C, D, E
Coal flow, klb/hr	418	415	412
Boiler O ₂ , %	3.2	3.7	2.7
Air preheater inlet gas temp, F	777	774	747
CEMS data			
CO ₂ , % wet	9.4	10.0	10.2
SO ₂ , lb/MMBtu	0.12	0.11	0.12
NO _x , lb/MMBtu	0.44	0.34	0.37
Opacity, %	3.5	3.6	3.3
Stack flow, kwscfh	76,300	76,000	74,600
Scrubber Data			
Scrubbers in service	A, B, D	A, B, D	A, B, D
Scrubbers out of service	C	C	C
Scrubber A			
Gas inlet temperature	285	296	273
Gas outlet temperature	156	165	143
Lime slurry flow	21	21	24
Ash slurry flow	85	92	78
Scrubber B			
Gas inlet temperature	270	283	259
Gas outlet temperature	152	164	140
Lime slurry flow	24	18	20
Ash slurry flow	92	94	84
Scrubber D			
Gas inlet temperature	264	277	252
Gas outlet temperature	141	143	140
Lime slurry flow	20	20	20
Ash slurry flow	88	98	67

2.2 Flue Gas Sampling Locations

Table 2-2 presents a summary of key inlet and stack sample location parameters. Individual discussions of the two locations are presented below.

Inlet Location

The inlet samples were collected at the outlets of the two air preheaters on Craig 3. Drawings of one air preheater location are shown in Figures 4-1a and 4-1b. Flue gas from the boiler exits through two air preheaters, travels through an 18-foot long duct from each air preheater, enters a plenum, and then travels to the operating scrubber modules through inlet ducts to each module. The air preheater exit duct was chosen for sampling rather than the module inlet ducts because there is insufficient vertical clearance at the inlet ducts.

Six of twelve sample ports were sampled in each duct. Total sample time was:

2 ducts x 6 ports/duct x 5 points/port x 2 ½ minutes/point = 150 minutes.

This traverse pattern did not allow the Ontario Hydro requirement of a minimum of five minutes per sample point to be met. The exception to the Method was approved by William Grimley of the EPA.

This location does not meet the requirements of EPA Method 1. Cyclonic flow tests were performed in both air preheater exit ducts. The average cyclonic flow angle was less than 2 degrees, with no points having a cyclonic flow angle greater than 5 degrees.

Stack Location

The stack samples were collected at the existing stack sample ports. A schematic and cross section of the stack location is shown in Figure 4-2.

Sample time at the stack was 144 minutes, with 12 minutes/point at 12 points.

This location meets the requirements of EPA Method 1. Cyclonic flow testing showed the cyclonic flow angle to be less than 5 degrees at all traverse points.

The flue gas at the stack is below the method specification of a minimum filtration temperature of 120°C. Therefore, heated filtration per Method 5 was used, with a minimum probe and filter temperature of 120°C.

Table 2-2. Craig Unit 3 Sampling Location Descriptions

	Inlet	Stack
Description	Both APH outlet ducts	Stack platform
Elevation	Approximately 100'	300'
Physical access	Elevator, stairs	Elevator
Side or top access	Top	Side
Round or rectangular	Rectangular	Round
Port length (outside of port to inner stack wall)	18"	18"
Number/type of ports	Six 4-inch w/ flanges	Four 4-inch w/ threaded plugs
Inside dimensions	Each duct 8' 6" deep x 34' 6" wide Equivalent diameter 13.6'	24' 11 1/2" ID
Nearest upstream disturbance		
Disturbance	Right angle turn	Duct entrance
Distance, ft	17'	200'
Distance, diameters	1.3	8
Nearest downstream disturbance		
Disturbance	Entrance to plenum	Stack exit
Distance, ft	1'	300'
Distance, diameters	0.1	11

2.3 Coal Sampling Location

Coal samples were collected from the silo just above the coal feeders to each operating mill. The lag time for coal to travel from the sample location to the boiler is approximately two minutes. One one-pint jar sample was collected from each mill during the first and last hour of each test run, and all samples were composited. Samples were collected by Mr. John Mihalich of Craig Station.

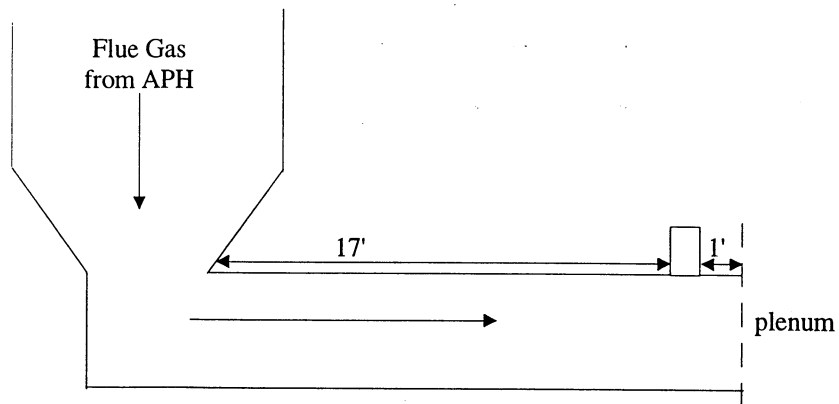


Figure 2-2a. Craig Unit 3 Inlet Sampling Location

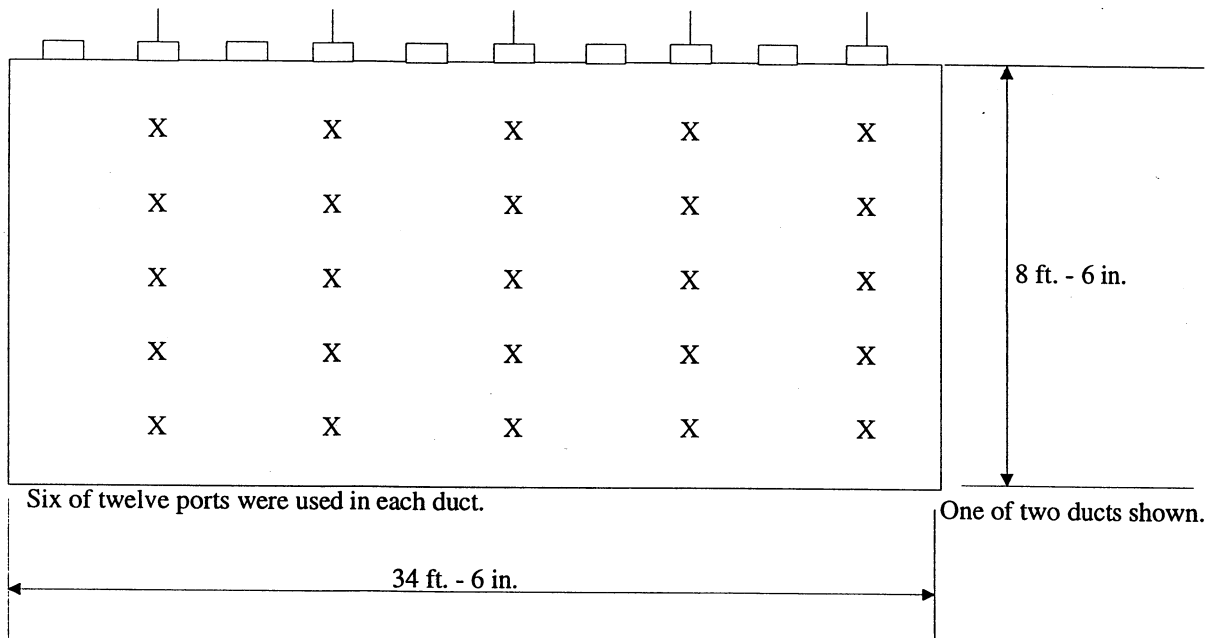
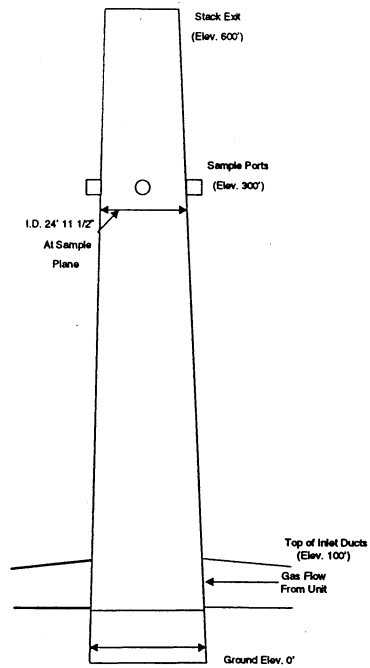
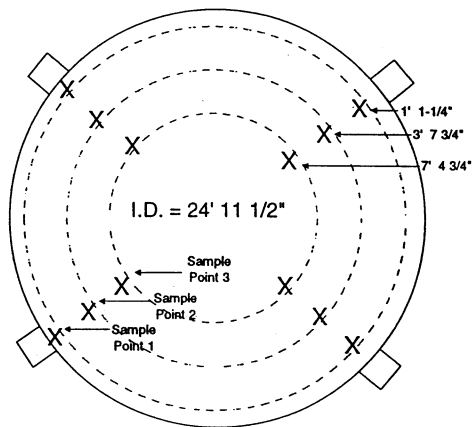


Figure 2-2b. Craig Unit 3 Inlet Sampling Location



a. Diagram of Stack



b. Cross-Section of Sample

Figure 2-3. Craig Unit 3 Stack Sampling Location

3

SUMMARY AND DISCUSSION OF TEST RESULTS

3.1 Objectives and Test Matrix

Objectives

The objective of the program is to collect the information and measurements required by the EPA Mercury ICR. Specific objectives are:

- Quantify speciated mercury emissions at the stack.
- Quantify speciated mercury concentrations in the flue gas at the scrubber inlet.
- Quantify fuel mercury and chlorine content during the stack and inlet tests.
- Provide the above information for use in developing boiler-, fuel-, and control device-specific mercury emission factors.

Test Matrix

The test matrix is presented in Table 3-1, and actual test times are shown in Table 3-2. Table 3-1 includes a list of test methods used. In addition to speciated mercury, the flue gas measurements included moisture, stack gas flow, and O₂/CO₂.

3.2 Field Test Changes and Problems

Coal Mercury Analysis – Change of Laboratory and Analytical Method

The test plan called for coal mercury analysis to be performed by Philip Analytical, using EPA SW846. However, the results for all three samples came back as ND<0.04 ppm, the stated detection limit for SW846.

In order to achieve lower detection limits splits of the samples were sent to Frontier Geosciences for analysis by cold vaporatomic fluorescence (modified EPA 1631), following digestion by cold aqua regia (modified EPA 7371). These results provided detectable levels of mercury below 0.04 ppm, and are used as the reported coal mercury values.

Table 3-1. Test Matrix for Mercury ICR Tests at Craig 3

Sampling Location	No. of Runs	Species Measured	Sampling Method	Sample Run Time	Analytical Method	Analytical Laboratory
Stack	3	Speciated Hg	Ontario Hydro	150 min	Ontario Hydro	Philip Services
Stack	3	Moisture	EPA 4	Concurrent	Gravimetric	FERCo
Stack	3	Gas Flow	EPA 1/2	Concurrent	Pitot Traverse	FERCo
Stack	3	O ₂	Batch Sample	Concurrent	Portable O ₂	FERCo
Stack	3	CO ₂	N/A	Concurrent	Plant CEMS	FERCo
Inlet	3	Speciated Hg	Ontario Hydro	144 min	Ontario Hydro	Philip Services
Inlet	3	Moisture	EPA 4	Concurrent	Gravimetric	FERCo
Inlet	3	Gas Flow	EPA ½	Concurrent	Pitot Traverse	FERCo
Inlet	3	O ₂	Batch Sample	Concurrent	Portable O ₂	FERCo
Inlet	3	CO ₂	N/A	Concurrent	Dilution calc	FERCo
Coal Feeders	3	Cl in coal	Modified ASTM D2234	1 grab sample per coal feeder per run	EPA SW 846: 7471A (Hg) 5050/9056 (Cl)	Philip
Coal Feeders	3	HHV, Ash, S, Moisture	Modified ASTM D2234	1 grab sample per coal feeder per run	ASTM D514290	CTE
Coal Feeders	3	Hg in coal	Modified ASTM D2234	1 grab sample per coal feeder per run	Modified EPA 7371/1631	Frontier Geosciences

Table 3-2. Craig Unit 3 Sampling Times

Run No.	1	2	3
Date, 1999	4-Oct	4-Oct	5-Oct
Inlet Tests			
Start time	0921	1335	0836
Stop time	1233	1636	1142
Total sample time, min	150	150	150
Stack Tests			
Start time	0930	1335	0830
Stop time	1219	1629	1120
Total sample time, min	144	144	144
Notes:			
1. Gas flow, moisture, O ₂ were concurrent with mercury tests.			
2. Coal samples were collected during the first and last hour of each run.			

Holding Time

Due to scheduling problems in the laboratory, the particulate fractions of the samples were analyzed 47 to 48 days after sampling. The Ontario Hydro Method specifies 45 days.

This discrepancy is not considered to have any impact on the results. Dennis Laudal of the University of North Dakota (the author of the Ontario Hydro Method) indicates that they have performed stability studies showing that samples are stable for at least 3 months.

3.3 Presentation of Results

The test results are presented in the following tables and figure:

- Table 3-3. Sample gas conditions.
- Table 3-4. Mercury concentration and speciation results.
- Table 3-5. Mercury removal across scrubber by species.
- Figure 3-1: Mercury speciation across scrubber system.

Results are calculated as $\mu\text{g}/\text{sm}^3$ (at a reference temperature of 68°F), and normalized for dilution by converting to a $\text{lb}/10^{12}$ Btu basis. This method allows direct comparison of inlet and stack results without incorporating uncertainties involved in gas flow measurement.

Table 3-3. Craig Unit 3 Sample Gas Conditions

	Run 1	Run 2	Run 3	Average
Test Date	4-Oct	4-Oct	5-Oct	
Inlet Gas Properties				
Temperature, F	280	294	271	281
Gas flow, dscfm	971,626	972,331	973,518	972,579
Comparison gas flows, dscfm				
Pitot traverse	1,058,631	1,077,973	1,095,201	1,077,268
Calculated from fuel input and O ₂	1,033,826	1,017,339	994,927	1,015,364
Calculated from fuel input and CO ₂	1,082,329	1,014,987	991,005	1,029,441
O ₂ , %	6.57	6.36	6.36	6.43
CO ₂ , %	12.05	12.84	12.86	12.58
H ₂ O, %	9.74	9.13	8.66	9.18
Stack Gas Properties				
Temperature, F	177	186	175	179
Gas flow, dscfm (corrected pitot traverse)	1,116,595	1,119,502	1,099,967	1,112,021
Comparison gas flow, dscfm				
Calculated from fuel input and O ₂	1,188,076	1,171,322	1,124,157	1,161,185
Calculated from fuel input and CO ₂	1,243,816	1,168,614	1,119,726	1,177,385
Stack CEMS	1,139,618	1,136,231	1,114,568	1,130,139
O ₂ , %	8.43	8.27	8.03	8.24
CO ₂ , %	10.49	11.15	11.38	11.01
H ₂ O, %	10.38	10.30	10.36	10.35

Table 3-4. Craig Unit 3 Mercury Speciation Results

	Run 1	Run 2	Run 3	Average
Test Date	4-Oct	4-Oct	5-Oct	
Inlet Mercury Speciation				
Particulate mercury				
ug/dscm	0.46	0.75	0.73	0.65
lb/10 ¹² Btu	0.41	0.66	0.64	0.57
% of total Hg	40%	58%	71%	56%
Oxidized mercury				
ug/dscm	0.52	0.41	0.19	0.37
lb/10 ¹² Btu	0.46	0.36	0.17	0.33
% of total Hg	46%	31%	19%	32%
Elemental mercury				
ug/dscm	0.16	0.14	0.10	0.13
lb/10 ¹² Btu	0.14	0.13	0.09	0.12
% of total Hg	14%	11%	10%	12%
Total mercury				
ug/dscm	1.14	1.31	1.02	1.16
lb/10 ¹² Btu	1.02	1.14	0.89	1.02
Stack Mercury Speciation				
Particulate mercury				
ug/dscm	ND<0.005	ND<0.005	ND<0.005	ND<0.005
lb/10 ¹² Btu	ND<0.005	ND<0.005	ND<0.005	ND<0.005
% of total Hg	0%	0%	0%	0%
Oxidized mercury				
ug/dscm	ND<0.05	ND<0.05	ND<0.05	ND<0.05
lb/10 ¹² Btu	ND<0.05	ND<0.05	ND<0.05	ND<0.05
% of total Hg	0%	0%	0%	0%
Elemental mercury				
ug/dscm	0.63	0.63	0.59	0.62
lb/10 ¹² Btu	0.64	0.64	0.59	0.62
% of total Hg	100%	100%	100%	100%
Total mercury				
ug/dscm	0.63	0.63	0.59	0.62
lb/10 ¹² Btu	0.64	0.64	0.59	0.62
Coal Analysis				
Mercury, ppm dry	0.011	0.010	0.009	0.010
Mercury, lb/10 ¹² Btu	0.89	0.75	0.72	0.79
Chlorine, ppm dry	100	<100	200	117
Moisture, %	17.09	17.11	17.94	17.4
Sulfur, % dry	0.47	0.44	0.49	0.47
Ash, % dry	6.63	5.96	6.40	6.33
HHV, Btu/lb as fired	10,404	10,464	10,308	10,392
Coal flow, lb/hr as fired	418,000	415,000	412,000	415,000
Total Mercury Mass Rates				
lb/hr input in coal	0.0039	0.0033	0.0031	0.0034
lb/hr at baghouse inlet	0.0042	0.0047	0.0037	0.0042
lb/hr emitted	0.0026	0.0027	0.0024	0.0026

Table 3-5. Craig Unit 3 Mercury Removal Efficiency

Run No.	1	2	3	Average
Date, 1999	4-Oct	4-Oct	5-Oct	
Total mercury				
Inlet, lb/10 ¹² Btu	1.02	1.14	0.89	1.02
Stack, lb/10 ¹² Btu	0.64	0.64	0.59	0.62
Removal efficiency, %	37%	44%	34%	39%
Particulate mercury				
Inlet, lb/10 ¹² Btu	0.41	0.66	0.64	0.57
Stack, lb/10 ¹² Btu	ND<0.005	ND<0.005	ND<0.005	ND<0.005
Removal efficiency, %	100%	100%	100%	100%
Oxidized mercury				
Inlet, lb/10 ¹² Btu	0.46	0.36	0.17	0.33
Stack, lb/10 ¹² Btu	ND<0.05	ND<0.05	ND<0.05	ND<0.05
Removal efficiency, %	100%	100%	100%	100%
Elemental mercury				
Inlet, lb/10 ¹² Btu	0.14	0.13	0.09	0.12
Stack, lb/10 ¹² Btu	0.64	0.64	0.59	0.62
Removal efficiency, %	-350%	-408%	-577%	-426%

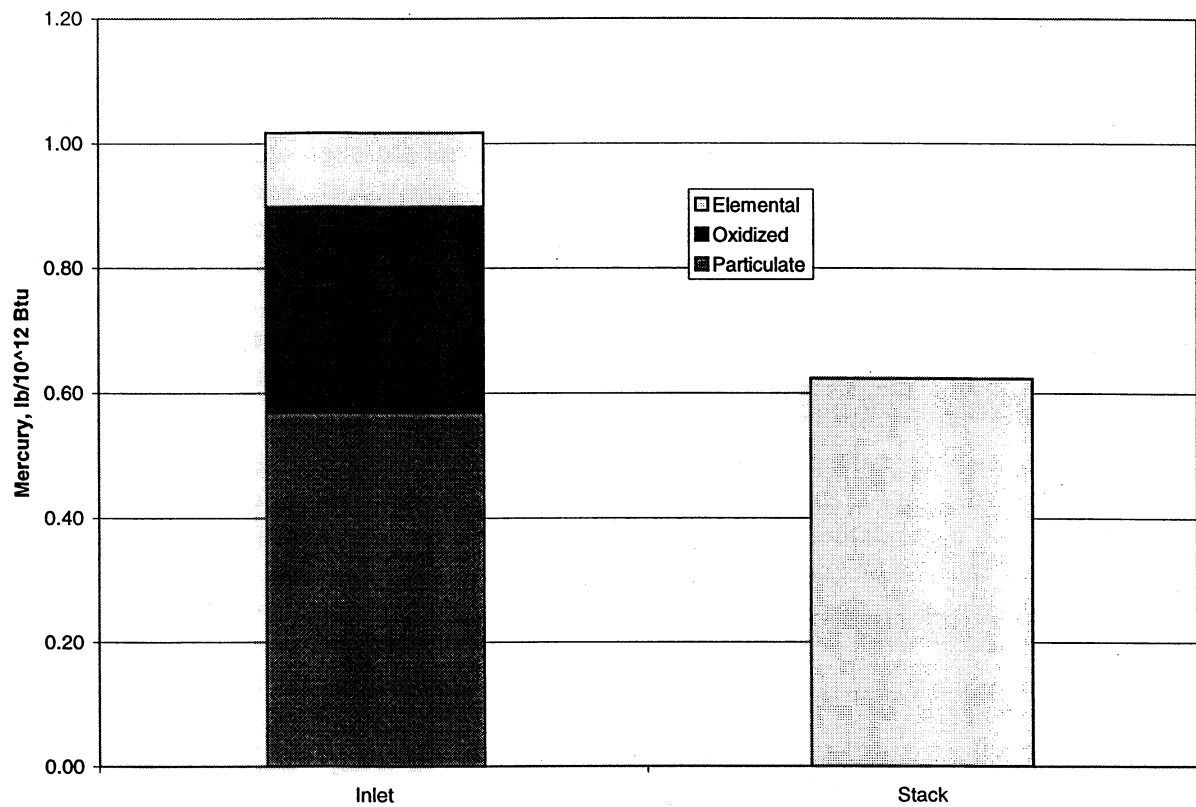


Figure 3-1. Mercury Speciation Across Craig Unit 3 Scrubber

Major observations that can be made from the results are:

1. At the inlet the measured mercury was primarily in the particulate phase (56% of total mercury), with 32% as oxidized mercury and 12% as elemental mercury. Agreement among the triplicate runs was good to excellent. Total mercury concentration was $1.0 \text{ lb}/10^{12} \text{ Btu}$.
2. At the stack only elemental mercury was detected, at a level of $0.62 \text{ lb}/10^{12} \text{ Btu}$. Scrubber removal efficiency for total mercury was 39%.
3. The results showed complete removal of oxidized and particulate mercury across the scrubber. However, measured elemental mercury increased by a factor of five across the scrubber. This apparent increase could be due to real scrubber mechanisms (such as conversion of oxidized or particulate mercury to elemental, or release of elemental mercury from the recycled flyash injected into the scrubber), or it could be an artifact of the sampling methodology at the inlet. Since the inlet location is upstream of the particulate control device, there is a large quantity of fly ash collected in the thimble filter at the front of the sample train. It is possible that gas phase oxidized and elemental mercury are absorbed on this fly ash during sampling, creating a positive bias in particulate mercury and a negative bias in gas phase mercury.
4. Mercury levels in the coal averaged 0.010 ppm or $0.79 \text{ lb}/10^{12} \text{ Btu}$, compared to $1.02 \text{ lb}/10^{12} \text{ Btu}$ total mercury at the inlet. The difference of 29% between the coal input and the inlet flue gas is not considered significant, given the low mercury levels and the uncertainties of the coal and flue gas measurement methods.

4

SAMPLING AND ANALYTICAL PROCEDURES

4.1 Test Methods

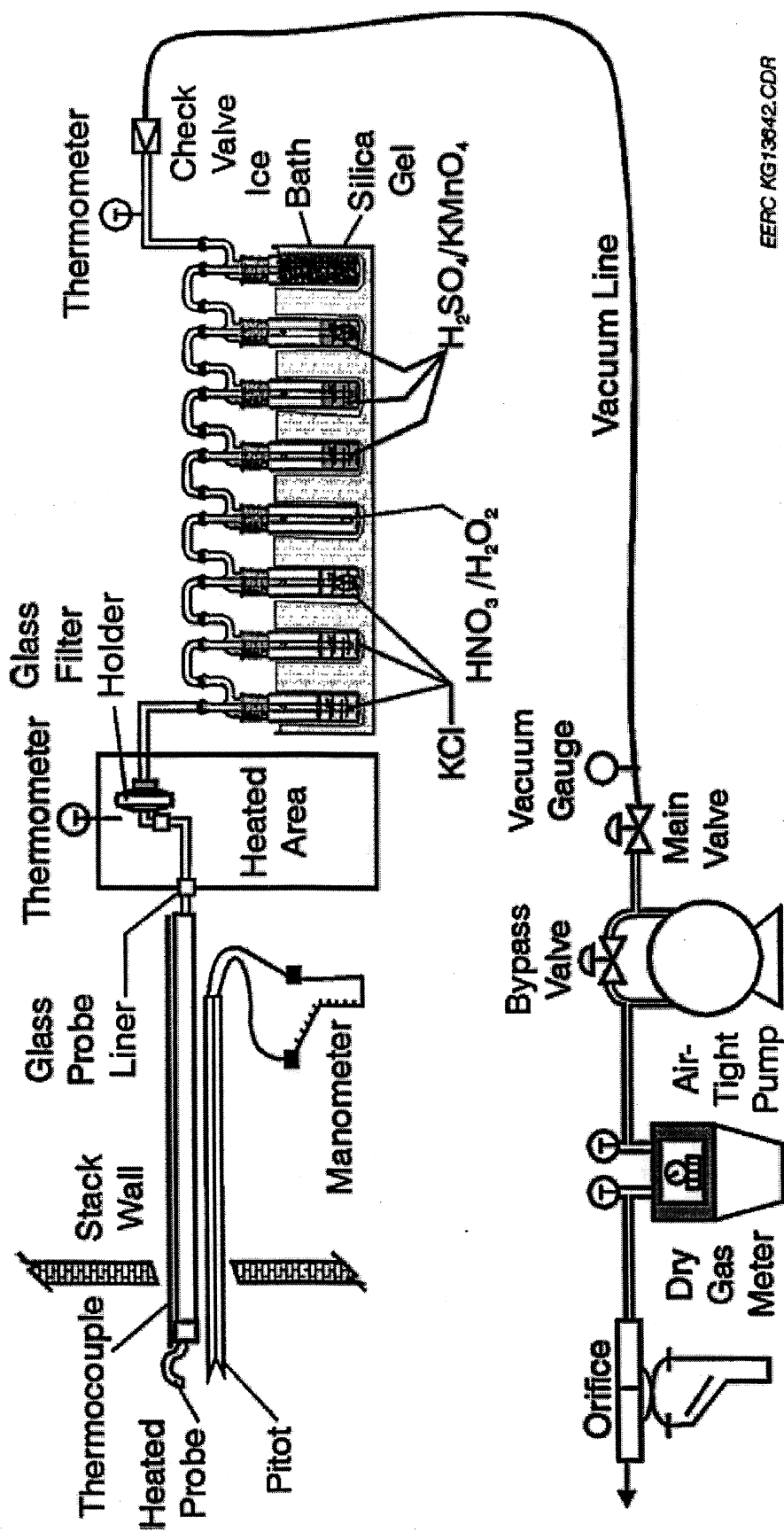
This section contains a summary of the sampling and analytical procedures used to conduct the mercury speciation required in EPA's ICR titled, "Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)" dated April 8, 1999. The full text of the method was presented as Appendix A of the Test Plan.

Subsequent to submittal of the Test Plan, additional drafts of the Ontario Hydro Method were published. Wherever possible, the new features of these drafts were incorporated into the program.

Speciated mercury samples were collected in three test runs at the inlet and outlet of the control device. The inlet and outlet sampling were concurrent. A field blank was collected at each test location on October 2, the set up day. The field blank consisted of assembling a sample train, transporting it to the sample location, conducting a leak check, letting the train sit for two to three hours, and then recovering the train as if it were a sample.

EPA methods to determine flue gas flow rate were used. EPA Reference Method 5 and 17 requirements for isokinetic sampling were followed. Each impinger was weighed before and after sampling to determine flue gas moisture content.

Figure 4-1 presents a schematic of the mercury speciation sample train, Table 4-1 presents a list of sample train components for the Method 17 configuration, and Table 4-2 presents a list of sample train components for the Method 5 configuration. The sampling train was set up with in-stack filtration (EPA Method 17 configuration) for the inlet location and external heated filtration (EPA Method 5 configuration) for the stack location.



EERC KG13642.CDR

Figure 4-1. Schematic of the Mercury Speciation Sample Train
(Method 5 option as used at the stack is shown; Method 17 in-stack filtration was used for the Inlet on Craig 3)

Table 4-1. Sample Train Components - Method 17 Configuration

Component	Details
Nozzle	Glass.
Filter	Quartz thimble, in glass thimble holder.
Probe	Teflon, heated to minimum 120 C.
Connector line	Heated teflon line used to connect from probe to impingers. Heated to minimum 120 C.
Impingers 1, 2	1 mol/l KCl solution; modified Smith Greenburg (SG) impinger.
Impinger 3	1 mol/l KCl solution; standard Smith Greenburg impinger.
Impinger 4	5% nitric acid/10% hydrogen peroxide; modified SG impinger.
Impingers 5, 6	4% potassium permanganate/10% sulfuric acid; modified SG impinger.
Impinger 7	4% potassium permanganate/10% sulfuric acid; standard SG impinger.
Impinger 8	Silica gel; modified Smith Greenburg Impinger

Table 4-2. Sample Train Components - Method 5 Configuration

Component	Details
Nozzle	Glass
Probe	Glass, heated to minimum 120 C.
Filter	Quartz, in glass holder, heated to minimum 120 C.
Filter support	Teflon.
Connector line	Heated teflon line used to connect from probe to impingers. Heated to minimum 120 C.
Impingers 1, 2	1 mol/l KCl solution; modified Smith Greenburg (SG) impinger.
Impinger 3	1 mol/l KCl solution; standard Smith Greenburg impinger.
Impinger 4	5% nitric acid/10% hydrogen peroxide; modified SG impinger.
Impingers 5, 6	4% potassium permanganate/10% sulfuric acid; modified SG impinger.
Impinger 7	4% potassium permanganate/10% sulfuric acid; standard SG impinger.
Impinger 8	Silica gel; modified Smith Greenburg Impinger

Sample was withdrawn from the flue gas stream isokinetically through the filtration system, which was followed by a series of impingers in an ice bath. Particulate-bound mercury was collected on the front half and filter; oxidized mercury was collected in impingers containing 1 N potassium chloride solution; and elemental mercury was collected in one impinger containing a 5% nitric acid and 10% peroxide solution, and in three impingers containing a solution of 10% sulfuric acid and 4% potassium permanganate. An impinger containing silica gel collected any remaining moisture.

The filter media was quartz fiber filters. At the inlet, a quartz thimble in a glass holder was used. At the stack, a 105 mm quartz filter in a glass filter holder was used. At the inlet the probe included a heated teflon line; at the stack a heated glass probe was used. An additional heated teflon line was used to transport the flue gas from the end of the probe to the inlet of the first impinger. Both the probe and the line were heated to maintain a minimum gas temperature of 248°F.

A 150 minute sampling time was used at the stack, with a target sample volume of 1 to 2.5 standard cubic meters. At the inlet, a sample time of 144 minutes was used.

Sample Recovery

Figure 4-2 is a schematic of the sample recovery procedure for the impinger train. The samples were recovered into precleaned glass bottles with vented teflon lined lids for shipment to the laboratory. The following sample fractions were recovered (specific rinse solutions are contained in the method):

1. The sample filter;
2. The front half rinse (includes all surfaces upstream of the filter)
3. Impinger 1 through 3 (KCl impingers) and rinses;
4. Impinger 4 ($\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) and rinses;
5. Impingers 5 through 7 ($\text{KMnO}_4/\text{H}_2\text{SO}_4$ impingers) and rinses;
6. Impinger 8 (silica gel impinger). Note this sample is weighed for moisture determination and is not included in the mercury analysis.

Sample Digestion and Analysis

The sample fractions were digested and analyzed as specified in the method and summarized below:

Ash Sample (Containers 1 and 2)

If the particulate catch is greater than 1 gram (as would be the case at most particulate control device inlet locations), an aliquot of the particulate collected on the filter is digested by microwave digestion.

KCl Impingers (Container 3)

The impingers are digested using H_2SO_4 , HNO_3 , and KMnO_4 solutions as specified in the method.

$\text{KNO}_3\text{-H}_2\text{O}_2$ Impinger (Container 4)

The impinger solution is digested using HCl and KMnO_4 solutions as specified in the method.

$\text{H}_2\text{SO}_4\text{-KMnO}_4$ Impingers (Container 5)

The impinger solution is digested using hydroxylamine sulfate as specified in the method.

Analysis

Each digested fraction is analyzed in duplicate for total mercury by cold vapor atomic absorption (CVAAS). CVAAS is a method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbency is measured as a function of mercury concentration. A soda-lime trap and a magnesium perchlorate trap must be used to precondition the gas before it enters the absorption cell.

1. Rinse filter holder and connector with 0.1N HNO_3 .
2. Add $\text{H}_2\text{SO}_4/\text{KMnO}_4$ to each impinger bottle until purple color remains.
3. Rinse with 0.1N HNO_3 .
4. Rinse with 8N HCl if brown residue remains.
5. Final rinse with 0.1N HNO_3 .

Rinse Bottles Sparingly with

- 0.1N HNO_3
- 8N HCl
- 0.1N HNO_3

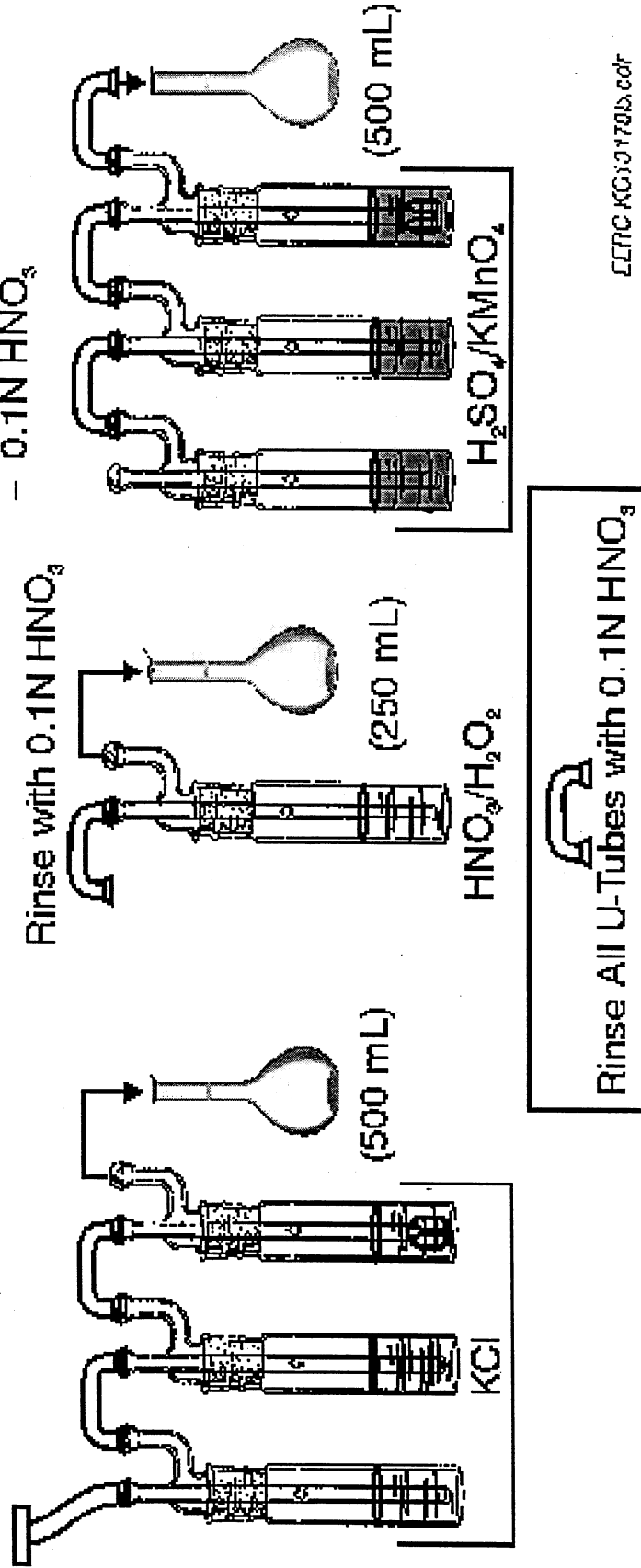


Figure 4-2. Sample Recovery Scheme for the Mercury Sampling Train

Handling of Non Detects

This section addresses how data was handled in cases where no mercury was detected in an analytical fraction.

A single analytical fraction representing a subset of a mercury species is not detected. When more than one sample component is analyzed to determine a mercury species and one fraction is not detected, it is counted as zero. This occurred on all of the samples for elemental mercury, which is the sum of the mercury collected in the $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger and the $\text{H}_2\text{SO}_4/\text{KMnO}_4$ impingers. For example, on Test 3-Stack the H_2O_2 fraction was $\text{ND}<0.25\ \mu\text{g}$ and the KMnO_4 fraction was $1.1\ \mu\text{g}$. Elemental mercury was reported as $1.1\ \mu\text{g}$.

No mercury is detected for a species on all three test runs. When all three test runs show no detectable levels of mercury for a mercury species, that mercury species is reported as not detected at less than highest detection limit. For example, the results for the three stack particulate mercury runs were all $\text{ND}<0.005\ \text{lb}/10^{12}\ \text{Btu}$. The average is reported as $\text{ND}<0.005\ \text{lb}/10^{12}\ \text{Btu}$.

In summing up individual species to determine total mercury, a value of zero is used for non-detected species. For example, the average stack mercury values (in $\text{lb}/10^{12}\ \text{Btu}$) were $\text{ND}<0.005$ for particulate mercury, $\text{ND}<0.05$ for oxidized mercury, and 0.62 for elemental mercury. Total mercury is reported as $0 + 0 + 0.62$, or 0.62 .

In calculating the percentage of mercury in each two species, a value of zero is used for the non-detected species. For the example listed in the preceding paragraph, the results are reported as 0% particulate mercury, 0% oxidized mercury, and 100% elemental mercury.

Auxiliary Flue Gas Measurements

Auxiliary flue gas measurements performed were flue gas flow rate per EPA Methods 1 and 2 (pitot traverse), O_2 by portable O_2 analyzer (as described below), and H_2O by EPA Method 4 (condensation/gravimetric analysis). These measurements were collected as integral parts of all mercury speciation test runs at both the inlet and stack locations.

Stack Flow Bias Correction

Previous studies at Craig have shown that S-type pitot probe measurements produce a false positive bias due to non axial flow, even though the degree of non axial flow is within the tolerance of Methods 5 and 17 for isokinetic sampling.

To correct for this bias, measured S-type pitot stack flow rates were multiplied by a correction factor to determine stack flow rates. The correction factors were obtained by comparison of 3-dimensional flow test results per Method 2F and S-type pitot measurements per Method 2 from the annual RATA program conducted prior to the ICR tests. The stack flow correction factor applied to the Craig 3 S-type pitot traverses was 0.948 .

Corrected stack flow results are used to report stack flow rate, and to calculate mercury emissions in lb/hr.

The gas velocity measurements were not corrected when used to establish isokinetic gas sampling rates, since the flow uncertainty is within normal Method 5 tolerances.

Inlet Flow Determination

There will typically be higher uncertainties in gas flow measurements at the inlet location relative to the stack location due to non axial flow. To calculate mercury levels in terms of lb/hr at the inlet, the outlet flow, corrected for dilution using O₂ measurements, was used for inlet values. This allows direct comparison of inlet and outlet mercury measurements without incorporating added uncertainty from the gas flow measurements.

Comparative Flow Rate Calculations

As a QA indicator, additional flow rate determinations were done. At both locations, exhaust gas flow was calculated based on boiler fuel input and both oxygen (F_d) and carbon (F_c) F factors. At the stack, the plant CEMS stack flow rate is presented. At the inlet the pitot traverse results, multiplied by two since only one of two ducts was tested, are presented in Table 3-3.

Alternate Methodology for O₂/CO₂ Determination

As an alternate to conventional Orsat analysis, the following procedure was used for determination of O₂ and CO₂ content.

O₂ determination. O₂ was measured by a portable O₂ analyzer using an electrochemical cell. The gas sample for the portable analyzer was drawn through a tube inserted in the exit gas of the sample gas meter. This provides direct analysis of the gas sampled for the mercury test. Care was taken that the O₂ sample tube was not inserted so far that it interfered with the meter orifice pressure differential reading. Calibration procedures for the portable analyzer included:

1. At the beginning of the test day, the instrument was calibrated on ambient air. As-found readings were then taken using zero gas and an EPA Protocol 1 mid scale O₂ calibration gas (40 to 60% of the span used to collect readings). If these as found readings were within 2% of span, the data was acceptable. If the readings were outside of these ranges, the O₂ cell was replaced, the instrument was repaired, or an alternate instrument was used.
2. During testing, the calibration of the instrument was checked on ambient air every three or four sample points. If the as-read value on air had drifted more than 0.2% O₂ (0.8% of scale), the instrument was recalibrated.
3. At the end of the test day, the calibration error step described in Step 1 above was repeated.

CO₂ determination. CO₂ is used for molecular weight determination. At the stack, CO₂ readings were taken from the plant CEMS. Since the CEMS readings are on a wet basis, they were converted to a dry basis using the moisture content measured by the mercury train.

At the inlet, the CO₂ was calculated via dilution calculations from the inlet O₂, the stack O₂, and the stack CO₂.

Determination of Scrubber Mercury Removal Efficiency

Scrubber removal efficiency was calculated according to Equation 1 below:

$$(1) \quad E = 1 - C_{\text{out}}/C_{\text{in}}$$

Where,

E = removal efficiency

C_{out} = Concentration at scrubber outlet

C_{in} = Concentration at scrubber inlet

It is important that the inlet and outlet values be corrected for air inleakage to provide results on a consistent basis. For this program, the correction was achieved by calculating mercury concentration in units of lb/10¹² Btu. Mass emission rates were not used because of the relatively high uncertainties associated with gas flow measurement.

4.2 Process Data

Process data was collected on computer logs set up by station personnel. Data collected included key boiler and scrubber operating parameters, and all CEMS data.

Prior to and during each test, unit operation was assessed by station personnel to assure that operating conditions were within project target ranges.

5

INTERNAL QA/QC ACTIVITIES

5.1 QA/QC Problems

There were no sampling related QA/QC problems. All KMnO_4 impingers were purple at the conclusion of each test.

5.2 QA Audits and Data Quality Objectives

QA audit samples were analyzed as specified in the Ontario Hydro Method and listed in Table 5-1. Data quality objectives are listed in Table 5-2. Table 5-3 presents audit results and compares data quality results with data quality objectives. Table 5-4 presents individual mercury fraction mass measurements, along with field blank results.

All data quality objectives were met, with the following exception:

The target of the results, all runs being within 35% of the mean, was not met for one of the three runs on oxidized mercury at the inlet.

This does not necessarily indicate a problem, just that there was more data scatter than hoped for. The cause could be either process, sampling, or analytical related.

Table 5-1. Audit Samples for Ontario Hydro Mercury Speciation

Audit Sample	Acceptance Criteria and Frequency	Reference
Known reagent spike	Every 10 samples.	Ontario Hydro Section 13.4.1
Certified reference ash	One per program.	Ontario Hydro Section 13.4.1

Table 5-2. Data Quality Objectives for Flue Gas Mercury Analyses

<i>Measure</i>	<i>Objective</i>	<i>Approach</i>
Accuracy	$\leq 10\%$ of sample value or $\leq 10\times$ instrument detection limit	Reagent blanks-analyze one blank per batch of each reagent
Accuracy	Field blank $\leq 30\%$ of sample value, or no greater than reagent blank; whichever is higher	Collect and analyze one field blank at inlet and one at outlet; criteria evaluated for each mercury species
Accuracy	$\pm 10\%$ of nominal value	One known reagent spike every ten samples
Precision, lab analysis	$\leq 10\%$ RPD	All laboratory samples analyzed in duplicate, every 10 th sample analyzed in triplicate
Completeness	$\geq 95\%$	Failed or incomplete tests to be repeated, if possible and practical

Table 5-3. Results Evaluation and Verification Checklist

Measure	Objective	Result
<i>Unit Operation</i>		
Unit operating conditions	No unusual conditions	Steady, normal operation
Air pollution control device operation	No unusual conditions	Steady, normal operation
<i>Sample Train Information</i>		
Trains leak checked before/after each test	<0.02 cfm	All tests passed
Pitot probes leak checked	Zero leakage	All tests passed
Probe, line, and filter temperature maintained	Minimum 120 C	All tests passed
Sample rate isokinetics	90-110%	98-102% at inlet 100-101% at stack
Sample volume	1-2.5 std cubic meters	1.5 m ³ at inlet 1.9 m ³ at stack
Post-test color of permanganate impingers	Purple	All tests passed
<i>Results/lab QA</i>		
Flow rate for triplicate runs	All runs w/in 10% of mean (adjusted for load)	All flows w/in 1% of mean at inlet and stack.
Stack temperature for triplicate runs	All runs w/in 5% of mean	W/in 3% at inlet W/in 2% at stack
Total mercury for triplicate runs	All runs w/in 35% of mean	W/in 13% at inlet W/in 5% at stack
Particulate mercury	All runs w/in 35% of mean	W/in 28% at inlet Not detected at stack
Oxidized mercury	All runs w/in 35% of mean	One run 48% below mean at inlet, one run 39% above mean, and one run 9% above mean Not detected at stack
Elemental mercury	All runs w/in 35% of mean	W/in 25% at inlet W/in 5% at stack
Sample and blank spikes	w/in 10% of value	All tests passed
Field blanks	<30% of measured values	See Table 5-4

Table 5-4. Craig 3 Sample Fraction Mercury Measurements

	Run 1	Run 2	Run 3	Average	Field blank	Field blank/ sample, %
Inlet, µg/sample						
Filter/probe wash (particulate Hg)	0.69	1.1	1.1	1.0	ND<0.080	ND
KCl fraction (oxidized Hg)	0.78	0.6	0.29	0.6	ND<0.10	ND
H ₂ O ₂ fraction (elemental Hg)	ND<0.25	ND<0.25	ND<0.25	ND<0.25	ND<0.25	ND
KMnO ₄ fraction (elemental Hg)	0.24	0.21	0.15	0.2	ND<0.050	ND
Stack, µg/sample						
Filter/probe wash (particulate Hg)	ND<0.010	ND<0.010	ND<0.010	ND<0.010	ND<0.010	ND
KCl fraction (oxidized Hg)	ND<0.10	ND<0.10	ND<0.10	ND<0.10	ND<0.10	ND
H ₂ O ₂ fraction (elemental Hg)	ND<0.25	ND<0.25	ND<0.25	ND<0.25	ND<0.25	ND
KMnO ₄ fraction (elemental Hg)	1.2	1.2	1.1	1.2	ND<0.050	ND

